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Studies on the preparation, properties and analysis of high purity yttrium oxide and yttrium metal at the Ames Laboratory

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Discussions of the separation of yttrium from the rare-earth elements by ion exchange, of comprehensive investigations of the preparation of yttrium fluoride, and of various ways of reducing the fluoride to the metallic state are presented. Chemical and spectrographic methods of analyzing yttrium and its compounds for oxygen and other impurities are described and comparisons made between the different methods.

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Disciplines

Chemistry

Authors

C. V. Banks, O. N. Carlson, A. H. Daane, V. A. Fassel, R. W. Fisher, E. H. Olson, J. E. Powell, and F. H. Spedding

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HIGH PURITY YTTRIUM OXIDE
AND YTTRIUM METAL AT THE
AMES LABORATORY

by

C.V. Banks, O.N. Carlson, A.H. Daane
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AMES LABORATORY
RESEARCH AND DEVELOPMENT REPORT
U.S.A.E.C.



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July 1959

Ames Laboratory

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Iowa State University of Science and Technology

F. H. Spedding, Director

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STUDIES ON THE PREPARATION, PROPERTIES AND ANALYSIS
OF HIGH PURITY YTTRIUM OXIDE AND YTTRIUM METAL AT
THE AMES LABORATORY

C. V. Banks, O. N. Carlson, A. H. Daane, V. A. Fassel,
R. W. Fisher, E. H. Olson, J. E. Powell and
F. H. Spedding

Abstract--The research and development work carried out at the Ames Laboratory on the chemistry and metallurgy of yttrium is described in detail in this report or companion reports to which references are herein made. Discussions of the separation of yttrium from the rare-earth elements by ion exchange, of comprehensive investigations of the preparation of yttrium fluoride, and of various ways of reducing the fluoride to the metallic state are presented. Chemical and spectrographic methods of analyzing yttrium and its compounds for oxygen and other impurities are described and comparisons made between the different methods.

A pilot plant process for producing tonnage quantities of yttrium metal is presented with detailed descriptions of the equipment and

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Quantities of high purity yttrium metal were prepared by vacuum distillation and by a salt extraction refining process. Yttrium metal containing 100 to 300 ppm oxygen is soft, ductile and easily fabricated at room temperature.

INTRODUCTION

The rare-earth elements have been a subject of intensive study in the Ames Laboratory since 1943. This work was instigated by Dr. F. H. Spedding and has been under his personal direction since its inception. The early work concentrated on methods of separating these elements in high purity in the form of their oxides. As quantities

of the light rare-earth oxides became available from this work, many of the rare-earth metals and their compounds were prepared and studied in the chemistry, metallurgy, physics and chemical engineering divisions of this laboratory. Further development of separation processes has made available considerable quantities of the heavy rare earths, and larger quantities still of yttrium, which is a major constituent of the parent ores.

Small scale preparations of yttrium metal permitted studies on some of the properties of this metal, some of which were found suitable to recommend its consideration for use in nuclear reactors. Among these properties are: (1) a reasonably low thermal neutron cross-section of approximately 1.2 barns; (2) a relatively high melting point; (3) a high degree of resistance to attack by liquid uranium and uranium alloys; and (4) a miscibility with other metals to form alloys possessing useful high temperature properties.

This work became a part of the Laboratory's program of preparing metals of nuclear interest. This program made available large quantities of uranium and thorium in the past. In response to requests from various divisions of the Atomic Energy Commission, a considerable amount of work has been done on methods of preparing yttrium metal. Some of

this work has appeared in AEC documents from this Laboratory, some in papers in scientific publications, while some appears only in research notebooks and internal reports or other documents with limited distribution. Members of the Ames Laboratory Staff have compiled this report to consolidate this work on all aspects of the problem of the preparation of yttrium metal. The report has been divided into several sections, and the names of the scientists appearing at the beginning of each section represent the men mainly responsible for the developments in that area. A number of graduate students also worked on this problem in association with these men, and their names appear on the individual papers that have been published in the scientific literature. A bibliography of the contributions from the Ames Laboratory is appended so the reader can pursue the subject further if he so desires.

PART I. RESEARCH AND DEVELOPMENT

1. Preparation of Yttrium Oxide

F. H. Spedding, J. E. Powell and H. R. Burkholder

1.1 History of Rare-Earth Separation at Ames

The first separations of rare earths at Ames were accomplished by eluting mixtures of rare earths down beds of cation-exchange resin with 5% citrate solution at relatively low pH's. This technique was successful for the separation of small quantities of either naturally occurring or radioactive rare earths and is still used for the isolation of rare-earth activities from fission products. The early work on citrate elutions at Ames was described in a series of Manhattan Project Reports dating from 1945 to 1947¹ and was summarized in a series of J. AM. CHEM. SOC. articles in 1947.² Concentrated citrate was not economical, however, for use in moderate or large-scale rare-earth separations. For this reason, the Ames Laboratory turned its attention to lower concentrations and higher pH's in order to make more effective use of the eluting agent. The citrate elution technique was gradually modified and improved and the scale of operations was increased.³⁻⁷ Although separations were performed successfully under many conditions, 0.1% citrate at a pH of 8.0 was

highly recommended for use on H^+ -state resin beds.^{6, 7} In spite of the fact that sizable amounts of many rare earths were isolated in pure form by elution with dilute citrate, the process proved inadequate in its ability to resolve Sm-Eu-Gd, Tb-Y-Dy and Yb-Lu mixtures. Consequently, the search for a better method was continued.

Basic studies were next undertaken to determine the individual stabilities of the complex compounds formed between the rare earths and ethylenediaminetetraacetic acid (EDTA),⁸ and a second ion-exchange process was developed using EDTA as the eluant.^{9, 10} The key to success in utilizing EDTA was the use of cupric ion as a retaining ion instead of hydrogen ion. Although most salts of EDTA are soluble in water, the acid form of the reagent is not. Hydrogen ion used as the retaining ion promotes the formation of the insoluble acid, but cupric ion forms a soluble chelate species with EDTA which passes on through the system.

EDTA has a much higher resolving power than citrate so that it is possible to isolate all the lanthanide rare earths and yttrium using this reagent. A comprehensive report describing the EDTA elution process was written in 1955.¹¹ Recently this report has been revised,

improved by the inclusion of new data and submitted for publication in the Chemical Engineering Progress Symposium Series.¹²

Stability constants were also measured for the complexes formed between the rare earths and N-hydroxyethylethylenediamine-triacetic acid (HEDTA).¹³ This reagent proved superior to EDTA for resolving Yb-Lu mixtures, as well as being capable of resolving the light rare earths and isolating yttrium.¹² With HEDTA it was found that yttrium elutes between samarium and neodymium rather than between dysprosium and terbium as it does with both citrate and EDTA. This behavior was subsequently used to advantage in isolating yttrium by a combination of solvent-extraction and ion-exchange procedures by one of the companies which has adopted the Ames Laboratory methods.

Considerable work was also done at an early date with another reagent, diethylenetriaminepentaacetic acid (DTPA), but it was found that a reversal occurred in the elution sequence which made the separation of the elements from samarium to lutetium very difficult. However, it was found that yttrium was resolvable and eluted between samarium and neodymium as in the case of HEDTA.

Early in 1956, the rare-earth group at Ames was notified that the United States Atomic Energy Commission was interested

in obtaining large quantities of pure yttrium. At that time, the Ames Laboratory had already developed a process for isolating yttrium by the ion-exchange method on a moderate scale. With six-inch-diameter columns, several hundred pounds of high purity Y_2O_3 had already been produced. In order to develop the process for large-scale production, the design and construction of 30-inch-diameter columns was undertaken. Almost simultaneously, a great number of industrial concerns became interested in the process and visited the Laboratory to learn the intimate details of the process. Subsequently, Lindsay Chemical, Michigan Chemical, Heavy Minerals, Dow Chemical, St. Eloi, Research Chemicals and Mitten Chemical installed ion-exchange units similar to those at Ames and began to produce yttrium. Every one of these companies used the Ames Laboratory Process or some modification of it. As a result, the yttrium industry is well established today. Since the principles of the separation of rare earths by the ion-exchange technique have been described in several previous publications by Spedding and Powell,^{6, 7, 12, 14} this report will describe primarily the large-scale processing and separation of yttrium from the other rare earths.

The Ames process consisted of eluting a mixture containing yttrium down a copper-state, cation-exchange resin bed with an ammonia

buffered solution of ethylenediaminetetraacetic acid (EDTA). It had previously been determined that a pH of 8.4 and an EDTA concentration of 0.015M were optimum for this separation.¹¹ For citrate elutions it had also been determined that fine particle size, slow flow rate and elevated temperatures were beneficial in rare-earth separations.³ It should be emphasized at this point that yttrium is not really a rare earth, although in many reactions it behaves like the rare earths. It was not known, therefore, whether or not elevating the temperature at which the ion-exchange process was carried out would be beneficial in the isolation of yttrium using EDTA. At this time, there was also some question whether large-diameter columns would function as efficiently as those of smaller diameter. Since the need for yttrium was urgent, it was decided to immediately construct a pilot plant, based on 30-inch diameter columns, which could produce in the neighborhood of 500 pounds of pure Y_2O_3 per cycle. A plant of this size would not only allow us to determine whether or not a diameter-wise scale-up was feasible, but would also produce a great deal of yttrium at a time when it was sorely needed for metallurgical research. The plant was also needed to serve as a model for those companies who might later desire to produce yttrium.

Consequently, a pilot plant was assembled which consisted of twelve 30-inch-diameter ion-exchange columns, each ten feet high and filled to a height of nine and one-half feet with hydrogen-state, 40-50 mesh Amberlite IR-120. These columns were constructed of type 316-ELC stainless steel and were insulated so that experiments could be performed at elevated temperatures. It was known, of course, that rubber-lined or plastic-lined equipment could be used at room temperature, but it was uncertain whether these materials would long endure at 60°C and above. A number of stainless steel tanks for preparing and storing the EDTA eluant were also acquired. A more complete account of the 30-inch pilot plant appears later in this report.

1.2 Processing Xenotime Sand

Xenotime sand was chosen as the source of yttrium, chiefly because of its availability. Electromagnetically concentrated xenotime obtained from the Heavy Minerals Company, Chattanooga, Tennessee, contains approximately 36% Y_2O_3 and 24% other rare-earth oxides. The remainder is largely P_2O_5 accompanied by traces of some common elements. It was established very quickly that this mineral could be opened readily on a large scale by the method developed at Ames for monazite,¹⁵ provided a slightly higher digestion

temperature and a longer reaction time were used. This digestion with sulfuric acid gave a sludge which, when leached with water and filtered, gave a rare-earth sulfate solution suitable for loading directly on ion-exchange columns.

1.3 Study of Optimum Elution Distance

The method of elution used previously on six-inch columns was to elute the band about one and a half times its length down a series of cupric-state resin beds at a fast flow rate (800 ml per minute) and to use one-fourth of this rate for another one and one-half displacements of the band before recovering the product.¹¹ This amounted to three displacements of the band prior to breakthrough and another displacement during recovery of the product. However, the theory of ion-exchange separation developed by Powell and Spedding^{11, 12} predicted that the dysprosium would move out of the yttrium band in two band lengths and the terbium would separate from the yttrium in three band lengths. Since terbium elutes after yttrium, it appeared that only two feet of development would be required for each foot of band originally laid down on the system before collecting the product. The terbium would receive the benefit of elution for three band lengths before all of the yttrium was recovered.

In order to establish a base for comparison, only three of the twelve 30-inch columns were loaded with rare earths for the first large-scale experiment. This left nine columns or three band lengths for development of the band. The elution was carried out at a constant flow rate of five liters per minute (the equivalent of 200 ml per minute on six-inch columns). Profiles showed that equilibrium in the yttrium-terbium overlap portion of the band was reached by the time the dysprosium band reached the bottom of the twelfth column and that the dysprosium-yttrium overlap portion reached equilibrium at an earlier point in the elution (after only two band lengths). This is exactly what was predicted by the theory developed earlier at the Ames Laboratory by Powell and Spedding,^{11,12} and it was apparent that the system could be loaded more heavily. Subsequently, a run was carried out in which four columns were loaded instead of three and the rare-earth mixture was eluted under identical conditions down eight columns instead of nine. Profiles of the developing band showed that this was the optimum loading for the system.

The effect of these two experiments was to reduce the cost of processing yttrium concentrates by twenty-five per cent. This information was made available to all companies interested in supplying pure yttrium and influenced the design of their plants.

1.4 Investigation of Flow Rate

The 30-inch columns were loaded with 40-50 mesh resin, instead of the much coarser 20-30 mesh resin used in the six-inch columns. It was apparent from the first two large-scale experiments that the resolutions of the dysprosium and yttrium and the yttrium and terbium on the 30-inch columns were better than had previously been obtained on the six-inch columns containing a coarser resin. The next two experiments were carried out, therefore, at double the flow rate used in the first two experiments. The faster flow rate resulted in only a slight decrease in the yields of pure yttrium obtained. From these results it appeared that flow rate is not as critical with fine resin beds as with coarser ones and that even faster flow rates could be used profitably on these columns. This information was also made available to the commercial chemical concerns before their plants were fully designed. Consequently, they used finer resin and, hence faster flow rates, than was customary in commercial applications of ion exchange. A considerable reduction in the cost of the finished product thereby resulted.

1.5 Effect of Temperature on Separation

It was well established that increasing the temperature of elution results in shortening the overlaps between fully developed adjacent

rare-earth bands when EDTA and citrate are used as eluants. For this reason, two identical runs were carried out at 60°C at a flow rate of ten liters per minute in order to establish whether or not the equilibrium overlaps between yttrium and its two nearest rare-earth neighbors would behave similarly. Analytical profiles taken during the two experiments showed that, while the yttrium-terbium separation took place more rapidly than at room temperature, the dysprosium-yttrium separation proceeded more slowly. As a matter of fact, it was necessary to add two additional columns to the series in order to obtain complete resolution of the dysprosium and yttrium. It appears that the value of the yttrium-EDTA stability constant shifts closer to the value of the dysprosium-EDTA stability constant as the temperature is increased. The result is that the dysprosium-yttrium separation factor decreases and the yttrium-terbium separation factor increases. The smaller dysprosium-yttrium separation factor, due to operating at higher temperature, requires that the band be eluted a greater distance to obtain complete resolution. However, when the elutions were completed down the additional columns it was noted that the yields of pure yttrium were slightly larger than those obtained in the runs performed in a similar manner at room temperature.

This effect was due to the improved HETP value at the higher temperature, but the gain in yield was nullified by the additional columns and eluant which were required. It does not appear advisable to operate above room temperature. The commercial processors were, therefore, informed that it was not practical to use elevated temperatures in the isolation of yttrium with EDTA; thus, they were able to avoid the expense of installing heating equipment and insulating their columns.

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2. Preparation of Yttrium Halides

F. H. Spedding, O. N. Carlson, A. H. Daane, E. Olson,

R. W. Fisher, F. A. Schmidt, D. Dennison and J. P. Cook

As halides are compounds of choice for use in the preparation of many of the reactive metals, the halides of yttrium have been of considerable interest as a starting material in the reduction process. The relative inertness toward moisture of many metallic fluorides compared to other halides is characteristic of yttrium fluoride, and as a result, the major emphasis has been upon the preparation of the fluoride, in quantity and in high purity.

Due to the vital role of yttrium fluoride in the preparation of yttrium metal, independent but related studies on the fluoride have been carried on by several different groups in the Laboratory. These include groups in the Metallurgy, Physical and Inorganic Chemistry, the Engineering and Services Sections and the Chemical Engineering Sections. The work of these various groups represents their individual approaches to the solution of a common problem.

The chloride, bromide and iodide of yttrium were also desired to provide variations in preparative techniques in an effort to achieve higher purity yttrium metal.

2.1 Preparation of YF_3 by Direct Hydrofluorination of Y_2O_3 in Stationary and Rotary Furnaces

The procedure which has been employed most successfully for preparing high quality YF_3 on a large scale consists of the direct hydrofluorination of Y_2O_3 by passing anhydrous HF gas over the salt at elevated temperatures. Since yttrium oxalate or yttrium oxide are obtained directly from the ion exchange separation step, the direct hydrofluorination of these salts was investigated. The development of this process has been described in a report by Carlson, Schmidt and Spedding¹ and in a series of metallurgy progress reports of the Ames Laboratory.²⁻⁶

The experimental details of the process, including studies of the conditions which give optimum conversion, such as the control of particle size, calcining temperatures and other variables, are described in this section. A detailed description of the large scale hydrofluorination equipment, its construction, operation and production capacity are presented in a later section of this report.

Several methods were used to evaluate the quality of the fluoride produced, all of which were indirect or relative evaluations since the

direct determination of oxygen in YF_3 had not been developed at the time that this work was done. Two principal methods have been employed in these studies. In one, the fluoride was converted to the metal and the oxygen content of the resulting yttrium was determined directly. If all other variables were held constant, a comparison could be made between different grades of fluoride. The second, and more widely used method, was the spectrometric determination of the oxygen/argon intensity ratio (OIR) resulting when the fluoride was arced in a chamber of argon. This is described in detail in Section 5.4 of this report.

From correlation of the earlier OIR values on the fluoride with the analyzed oxygen in yttrium metal described in Section 3.2.2, it was found that fluoride with OIR values of greater than 0.45 gave poor slag-metal separations in the reduction step and yielded metal of high oxygen content. For YF_3 with OIR values less than 0.45, good separations were achieved and yttrium metal of noticeably lower oxygen content was obtained. However, there was no consistent variation in the quality of the fluoride or the corresponding metal produced by YF_3 with OIR values from 0.25 to 0.45. These conclusions were also verified by later work as the spectrometric method was modified and improved.

Anhydrous YF_3 can be prepared by passing anhydrous hydrogen fluoride over the oxide at elevated temperatures. The reaction is quite exothermic and good temperature control in the early stages of the hydrofluorinating cycle is difficult to maintain. Most of the early hydrofluorination studies were carried out in an electrically heated resistance furnace in which was inserted a monel retort with supporting shelves. Monel or inconel trays containing the Y_2O_3 were placed on these shelves. The inlet for the HF gas was located in one end of the retort so that the gas passed over each tray before leaving the furnace.

A number of variables immediately became apparent in attempting to prepare YF_3 by direct hydrofluorination of the oxide. An effort was made to study these variables and to obtain the hydrofluorinating conditions which gave most complete conversion.

The data obtained using a static bed of yttrium oxide for a single hydrofluorinating cycle are presented in Table I. Ames Laboratory oxide which had been calcined at 800-900°C was used in this study. As can be seen from the fluorine analyses in the table, a single hydrofluorination cycle in the static bed gives nearly complete conversion to the fluoride. This treatment results in a conversion of better than

99.5%. However, since the objective of this work was the preparation of yttrium of low oxygen content, YF_3 of the maximum purity attainable was required. A single hydrofluorination was found neither to give reproducible results nor to produce fluoride with oxygen intensity ratios of less than 0.45.

Table I

Effect of Hydrofluorination Temperature Upon

the Conversion of Y_2O_3 to YF_3

Total Time of HF Cycle	Time at Max. Temp.	Max. Temp.	OIR of YF_3	% Fluoride (Theo. 39.06%)
8 hrs.	6 hrs.	575°C	0.47	---
8 hrs.	6 hrs.	575°C	0.43	39.04%
8 hrs.	6 hrs.	600°C	----	39.18%
10 hrs.	8 hrs.	575°C	0.46	39.03%
10 hrs.	8 hrs.	600°C	0.60	---
10 hrs.	8 hrs.	600°C	0.49	---
10 hrs.	8 hrs.	600°C	0.63	---
10 hrs.	8 hrs.	575°C	0.53	38.88%

It was found that repeated hydrofluorination in the stationary unit gave a consistently better grade of fluoride as indicated by data in Table II. Prior to the second HF treatment, the fluoride was removed from the trays and thoroughly mixed. These experiments indicated that a more uniform and improved quality of fluoride is obtained as a result of mixing and continued hydrofluorination.

Table II
Effect of a Second Hydrofluorination Treatment on OIR of YF_3

OIR after 1st 8 hr. Cycle	Max. Temp. of 2nd Cycle	OIR after 2nd 8 hr. Cycle
0.60	600°C	0.40
0.50	600°C	0.40
0.45	600°C	0.45
0.65	600°C	0.50

A series of experiments was then run to determine if the temperature at which the oxalate is calcined to the oxide has any effect upon the rate and efficiency of fluoride conversion. The entire series of

oxides was hydrofluorinated simultaneously so that no additional variable was introduced during this operation. The hydrofluorination was carried out in the stationary furnace under the conditions indicated in Table III.

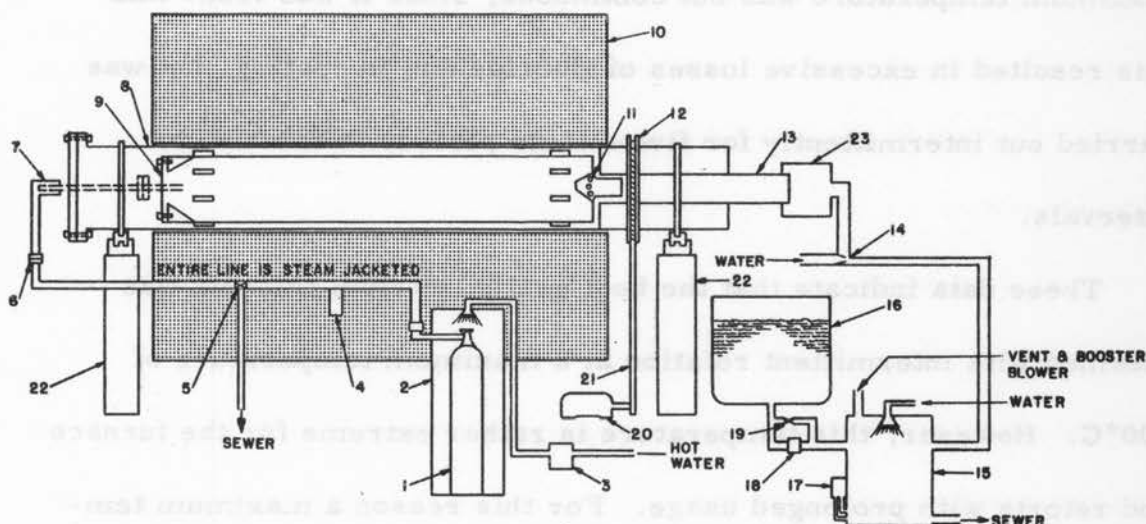
Table III
Effect of Calcining Temperature of Y_2O_3 on
Conversion to YF_3

Temp. of Calcination to Yttrium Oxide (22 hrs.)	% Loss on Ignition	OIR of YF_3	
		After 6 hrs. at 600°C.	Additional 6 hrs. at 600°C
600°C	58%	0.60	0.40
700°C	61%	0.50	0.40
800°C	60%	0.45	0.45
900°C	61%	0.35	0.40

The results of these experiments are interpreted as showing that oxide which has been ignited at 900°C is most readily converted to fluoride as indicated by the trend toward lower intensity ratio after six hours at 600°C. For these reasons it is recommended that the oxalate be ignited at 800 to 900°C. Again, repeated hydrofluorination produced a fluoride of uniform quality having an OIR of less than 0.45.

Since the stationary bed furnace apparently requires a dual cycle in order to obtain a grade of fluoride that is satisfactory for metal reduction, experiments were made using a rotating bed in place of the static bed. A schematic drawing of the rotary batch hydrofluorination furnace is shown in Fig. 1. The unit consists of a 12" outer inconel tube which serves as the support for an inner inconel tube or liner containing the Y_2O_3 . The liner is equipped with horizontal fins on the inside in order to increase the agitation of the powder. A conical shaped trap at the exit end of this chamber prevents excessive loss of material as dust in the exit gas stream. The exit gases are scrubbed by a water spray and passed into a neutralizing tank where a soda ash neutralizing solution is added. The entire tube assembly is surrounded by an electrically heated resistance furnace equipped with calrod heater elements. This furnace is capable of reaching a temperature of $900^{\circ}C$. The other details of the diagram are control features and engineering details.

Batches of yttrium oxide up to 50 lbs were run in the rotary furnace. It was found that continual rotation (20 rpm) was not feasible during the hydrofluorination cycle since considerable amounts of water present in the early stages caused the fluoride to form lumps. It is



- | | | |
|----------------------------------|-----------------------|------------------------------------|
| 1. HYDROGEN FLOURIDE CYLINDER | 9. INCONEL INNER TUBE | 16. SODA ASH NEUTRALIZING SOLUTION |
| 2. SPRAY CHAMBER | 10. ELECTRIC FURACE | 17. BECKMAN PH METER |
| 3. SOLENOID CHAMBER | 11. DUST TRAP | 18. VALVE TO PH CONTROLLER |
| 4. MANOMETER | 12. CHAIN SPROCKET | 19. BY-PASS VALVE |
| 5. CHECK VALVE | 13. NICKEL EXIT TUBE | 20. 1 H.P. A.C. MOTOR |
| 6. UNION | 14. WATER ASPIRATOR | 21. CHAIN |
| 7. TEFLON UNIVERSAL SEAL (INLET) | 15. NEUTRALIZING TANK | 22. BEARING SUPPORTS |
| 8. INCONEL OUTER TUBE | | 23. TEFLON UNIVERSAL SEAL(OUTER) |

Fig. 1. Furnace and Rotary Equipment for Hydrofluorination of Y_2O_3 .

believed that the formation of lumps prevents the hydrogen fluoride gas from coming into intimate contact with the oxide inside, and high intensity ratios on the fluoride are the result. The intensity ratios of fluoride prepared at various temperatures and rotation times in the rotary furnace are given in Table IV. The rotation cycle at the maximum temperature was not continuous, since it was found that this resulted in excessive losses of fluoride due to dusting, but was carried out intermittently for five-minute periods at ten-minute intervals.

These data indicate that the best quality yttrium fluoride was obtained with intermittent rotation at a maximum temperature of 800°C . However, this temperature is rather extreme for the furnace and retorts with prolonged usage. For this reason a maximum temperature of 750°C has been set for regular production work. This has resulted in an increased life of the heating elements of the furnace without affecting the quality of the fluoride adversely.

A few experiments were carried out on the direct hydrofluorination of yttrium oxalate trihydrate as a means of eliminating the calcining step. Yttrium oxalate was placed in a stationary bed hydrofluorination furnace and heated for six hours at 600°C in a

Table IV

Study of Rotation Cycle During Hydrofluorination and
Effect Upon Quality of Fluoride Produced

Maximum Temp.	Time at Max. Temp.	Rotation Cycle	Texture Product	OIR of Fluoride
700°C	5 hrs.	Intermittent for 3 hrs. at max. temp.	Powder	0.50
725°C	4 hrs.	"	Powder	0.40
750°C	4 hrs.	Intermittent for entire 8 hr cycle	Sintering & lump formation	0.55
750°C	4 hrs.	Intermittent for 3 hrs. at max. temp.	Powder	0.30
800°C	4 hrs.	"	Powder	0.35
800°C	4 hrs.	"	Powder	0.30
800°C	4 hrs.	1 hr. before max. temp., 4 hrs. after	Some lump formation	0.35
800°C	4 hrs.	2 1/2 hrs. at max. temp.	Powder	0.30
800°C	4 hrs.	"	Powder	0.30
800°C	4 hrs.	2 hrs. at max. temp.	Powder	0.35
800°C	4 hrs.	"	Powder	0.35

stream of anhydrous hydrogen fluoride gas. The resulting fluoride had an OIR of 0.50.

Another portion of the oxalate was hydrofluorinated for six hours at 800°C in a small rotary hydrofluorination unit with continuous rotation during the entire cycle. The OIR of the fluoride prepared in this manner was 0.40. Yttrium metal prepared from this fluoride contained 200-300 ppm carbon, indicating complete decomposition of the oxalate had occurred during the treatment. The capacity of the hydrofluorinating unit is considerably decreased when the oxalate is treated directly, due to its fluffiness and low packing density.

2.2 Preparation of YF_3 by Vibrating-Tray Type Hydrofluorination

Furnace

In an attempt to develop a method for producing tonnage quantities of YF_3 , a vibrating-tray furnace was designed and constructed. This furnace operated on the principle of a continuous flow of materials in which Y_2O_3 was introduced into one end of the system and anhydrous HF gas at the other. The details of the design of this apparatus and the results of the experiments are described in a report by Olson and Fisher.⁷

The reactor consisted of four inclined vibrating trays fixed in a cascade arrangement, allowing solids to flow at a controlled rate counter-current to the flow of anhydrous hydrogen fluoride gas. Temperature, pressure and feed rates were varied in the course of the experiments.

The test results indicated that although a completely satisfactory performance was not achieved, certain aspects appeared promising. The furnace provided a convenient method of handling the reactants; the actual operations were quite routine. Also, it was found that increasingly better yields were obtained on single passes at higher temperatures. A conversion of 99.13% was obtained on a single pass at 700°C.

The results of repeated tests, cycling of temperatures, and various design and construction alterations eventually exceeded the fatigue limits of the reactor and resulted in final dismantling of the equipment.

It was concluded from these experiments that a continuous process is feasible where very large amounts of material are required. However, it was shown by these experiments that operating conditions and the design of components are critical and that considerably more development work is needed before such equipment can be designed.

2.3 Preparation of Low Oxygen Content Yttrium Fluoride

Smutz, et al.⁸ have described experiments on the preparation of low oxygen content yttrium fluoride by the reaction of various yttrium compounds with anhydrous hydrofluoric acid. The compounds used were the oxide, hydrated fluoride, oxalate, chloride, nitrate, sulfate and sulfide of yttrium. Samples were hydrofluorinated in a static bed using a flow of anhydrous hydrofluoric acid at temperatures between 200 and 800°C.

The preparative methods which resulted in YF_3 with the lowest oxygen content were the drying of the hydrated yttrium fluoride in a stream of anhydrous hydrofluoric acid at 600°C, and the hydrofluorination of yttrium oxide in a platinum container under a flow of anhydrous hydrofluoric acid at 600°C. Both of these methods resulted in a low oxygen content yttrium fluoride with an oxygen intensity ratio of 0.35 or less.

Small scale purification methods investigated were: hydrofluorination of molten YF_3 , vacuum distillation and inert gas sparging. Yttrium fluoride specimens of varying oxygen content were used in the investigation. Yttrium fluoride with an OIR ratio of 0.20 to 0.35 was obtained by the HF treatment of the molten fluoride and also by vacuum distillation.

However, the high temperatures and difficult container problems limit the use of these methods to the preparation of small quantities of fluoride.

2.4 Preparation of Yttrium Fluoride by Ammonium Bifluoride Process⁹

The preparation of yttrium fluoride from the oxide, using ammonium bifluoride, was investigated quite thoroughly on a small scale. One-hundred-gram charges of yttrium oxide were reacted at different temperatures with various amounts of ammonium bifluoride in a closed graphite cylindrical crucible. It was found that yttrium fluoride with a fairly low OIR value (0.35) could be prepared from the oxide by reacting 7:1 and 9:1 mole ratio mixtures of ammonium bifluoride and yttrium oxide for two hours at 230°C and 130°C, respectively. The crucible was then sparged with argon at 400°C to remove reaction products and excess ammonium bifluoride.

The use of a vacuum during the two-hour oxide conversion period was also investigated, but the only set of conditions which gave low OIR fluoride (0.30 to 0.45) was a 7:1 mole mixture of ammonium bifluoride and yttrium oxide heated for two hours at 100-110°C, followed by sparging with argon to remove the excess ammonium fluorides.

The process was scaled up to enable reaction of a 4 lb charge of yttrium oxide. Duplicate runs were made using a 7:1 mole ratio of ammonium bifluoride to yttrium oxide at 230°C and a 9:1 mole ratio at 130°C. For the two 7:1 ratio runs at 230°C the average oxygen intensity ratio of six samples taken at different vertical and radial positions in the charge was 0.40 and 0.45. For the two 9:1 ratio runs the average OIR value was 0.30.

The fluorides obtained from the latter experiments were reduced to metal by the standard calcium reduction method. The oxygen contents of the resulting yttrium were 2420, 2470, 2620, and 2740 ppm for the yttrium fluorides with oxygen intensity ratios of 0.30, 0.40, 0.35, and 0.45, respectively. For yttrium fluoride prepared by regular hydrofluorination of the oxide (OIR values of 0.30-0.35) the yttrium metal generally contained between 2000 and 2200 ppm of oxygen. This comparison indicates that the yttrium fluoride prepared with ammonium bifluoride was not quite as good as that obtained by direct hydrofluorination with anhydrous HF.

Although the use of ammonium bifluoride as a hydrofluorination agent for yttrium oxide has the advantages of lower operating temperature and easier handling, the oxygen content of the yttrium fluoride

and yttrium metal appear to be slightly higher, and since the highest quality of yttrium fluoride obtainable was desired, no further investigations were made or are planned.

2.5 Preparation of YF_3 by Precipitation from Aqueous Solution

Several different approaches to the preparation of yttrium fluoride by the aqueous precipitation or "wet process" method were investigated. The method involves the precipitation of $\text{YF}_3 \cdot 1/2\text{H}_2\text{O}$ crystals from an aqueous solution by the addition of hydrofluoric acid, followed by a thermal decomposition step to remove the hydrated water.

One such approach was reported by Carlson, et al.¹ in which yttrium oxide was dissolved in hydrochloric acid and concentrated by evaporation to obtain crystals of $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$. Aqueous 70% HF was added to these crystals, forming the insoluble $\text{YF}_3 \cdot 1/2\text{H}_2\text{O}$.

Another method that was found to work satisfactorily was the addition of liquid anhydrous HF to a hot (100°C) yttrium chloride solution. The liquid HF was obtained by condensing the vapors in a copper coil immersed in a dry ice bath and allowing the condensate to drip into the hot chloride solution. The $\text{YF}_3 \cdot 1/2\text{H}_2\text{O}$ precipitate obtained in this manner was readily filtered. Smutz, et al.⁶ prepared $\text{YF}_3 \cdot 1/2\text{H}_2\text{O}$ by

precipitation with 48% hydrofluoric acid from an aqueous yttrium nitrate solution. The precipitate was centrifuged, washed and air dried.

The thermal decomposition of the hydrated fluoride was generally carried out by heating it in a stream of anhydrous HF gas. It was found that only partial dehydration is obtained at 300°C but that complete decomposition is accomplished by heating the hydrated fluoride slowly to 600°C. Small quantities of $\text{YF}_3 \cdot 1/2 \text{H}_2\text{O}$ were successfully dehydrated when dried in a stream of helium gas at 400°C at a pressure of 10 mm.

2.6 Preparation of YF_3 using Fluorine Gas

The preparation of low oxygen content yttrium fluoride using commercial fluorine gas was investigated by Tischer and Olson.¹⁰ Complete conversion of Y_2O_3 to YF_3 by the use of commercially pure fluorine was investigated. Fluorine was passed over the YF_3 samples at atmospheric pressure and room temperature and no lowering of the oxygen content was noted. In fact, it appeared that the oxygen content was slightly higher after fluorination than before. Subsequent runs at higher temperatures and pressures resulted in slight lowering

of the oxygen content of the fluoride. Yttrium fluoride with an initial oxygen intensity ratio of 0.45 fluorinated at 20 psi resulted in products with oxygen intensity ratios of 0.40, 0.35 and 0.35 for fluorination temperatures of 25, 600 and 700°C., respectively. Due to the high cost of the fluorine, difficult handling, and safety considerations, this method would not be practical for use in the preparation of large quantities of low oxygen content yttrium fluoride.

The fluorination of yttrium oxide, yttrium oxide-yttrium fluoride blend, and yttrium chloride did not yield a low oxygen content yttrium fluoride. No further investigations of the preparation of yttrium fluoride with fluorine are contemplated.

2.7 Yttrium Oxide-Yttrium Fluoride Equilibria

A study of the phase relationships in the yttrium oxide-yttrium fluoride system has been conducted by x-ray diffraction, thermal analysis and hydrolytic methods.

For x-ray and thermal analysis studies, samples were prepared by mixing stoichiometric quantities of YF_3 and Y_2O_3 , pressing these into pellets and sintering them in an atmosphere of argon gas at temperatures above 1000°C. The melting point of the sample was determined by slowly heating a pellet in which a hole had been drilled and observing the temperature at which this hole

filled with liquid and the temperature at which the pellet collapsed. Following such treatment, samples of the pellets were studied by x-ray diffraction. From this work, the following may be reported.

1. YF_3 is orthorhombic at room temperature, melts at 1154°C and undergoes a transformation at 1052°C .
2. Thermal analyses of samples containing 5, 9.5 and 15 mole % yttrium oxide showed the solid state transformation of YF_3 and an arrest at 1120°C that appears to be due to a eutectic.
3. A compound is present at 40 mole % Y_2O_3 that is the tetragonal β YOF, melting at 1920°C .
4. Alpha YOF (rhombohedral) is present at 50 mole % Y_2O_3 ; this melts at 2020°C .
5. A region of solid solubility appears to exist between 50 and 60 mole % Y_2O_3 .
6. A two phase region appears to exist between 60 and 100 mole % Y_2O_3 , apparently containing a eutectic of undetermined composition and temperature.

In working with these samples it was observed that when both forms of YOF were heated above 1500°C in a vacuum, they decompose to YF_3 and Y_2O_3 . Assuming that oxygen is present in YF_3 in the form of YOF, or a replacement of fluorine by oxygen occurs in the YF_3 lattice, a

distillation process was examined as a means of purifying YF_3 . The distillation was carried out on a small scale using gram quantities of YF_3 . A graphite crucible was used to contain the charge, and the fluoride prepared by hydrofluorination of Y_2O_3 was resistant to hydrolysis until a temperature of about 450°C was reached. The first step in the hydrolysis is the formation of $\beta\text{-YOF}$, a tetragonal crystal. No evidence of solid solution was found at high YF_3 concentration.

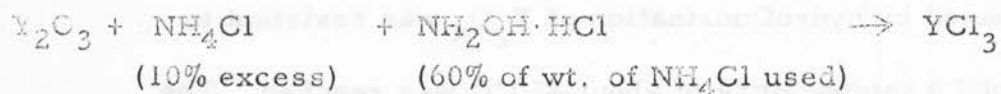
Since the hydrolysis experiment suggested that the hydrofluorination might be a two step process, a sample of incompletely converted oxide was secured and an x-ray powder pattern prepared. The pattern of this material containing 74% of the theoretical fluoride content showed the definite presence of $\beta\text{-YOF}$ along with YF_3 and some Y_2O_3 .

2.8 Preparation of Other Yttrium Halides

2.8.1 Yttrium Chloride

Several methods have been employed to prepare yttrium chloride in this Laboratory, the most successful being the dehydration of the hydrated chloride in a stream of dry hydrogen chloride gas. Other methods that have been examined in trying to find a more convenient preparative method are discussed below.

Yttrium oxide was heated with a 10% excess amount of ammonium chloride, with a quantity of hydroxylamine hydrochloride added to serve as the solvent medium:



After the YCl_3 was formed, the hydroxylamine hydrochloride was distilled away to leave the pure chloride. Analyses of the product showed it to contain 44.3 w/o yttrium (theoretical = 45.5%) and 51.6 w/o chlorine (theoretical = 54.5%). Less than 100 ppm Fe, Si, Cu, were present and rare earths were not detected. A thermal analysis of this material showed a melting point of 709°C .

Recently several pounds of YCl_3 has been prepared by passing HCl gas over yttrium metal turnings at 700°C and allowing the molten YCl_3 formed to drip and collect in a nickel vessel below. The chloride was then distilled under vacuum at 950°C to produce high quality YCl_3 . The analyzed oxygen content of this chloride was approximately 0.15 w/o oxygen.

Other less successful methods that have been studied for preparing yttrium chloride have been the dehydration of the hydrated yttrium chloride mixed with ammonium chloride in a stream of helium, and the reaction of carbon tetrachloride with Y_2O_3 .

2.8.2 Yttrium Bromide

Yttrium bromide has been prepared by heating a mixture of hydrated yttrium bromide and ammonium bromide slowly to 600°C in a stream of helium. Analysis of the product of this reaction showed it to contain:

Y - 26.6% (theoretical = 27.1%)

Br - 72.0% (theoretical = 72.9%)

Less than 100 ppm Fe, Si, and Cu and no detectable amounts of other rare earths were present. Thermal analysis of this material showed it to melt at 913°C.

2.8.3 Yttrium Iodide

Yttrium iodide was prepared by slowly heating a mixture of yttrium metal turnings and ammonium iodide to 700°C in a stream of helium. The resulting salt was vacuum sublimed in a tantalum apparatus to eliminate non-volatile impurities such as CaF_2 and YOF that may have been in the original product. Analysis of the salt showed it to contain 19.2 w/o yttrium (theoretical = 18.9%) and 80.3 w/o iodine (theoretical = 81.1%). Thermal analysis showed a melting point of 965°C.

Other methods that were studied for preparing yttrium iodide were:

1. The dehydration of hydrated YI_3 in the presence of NH_4I . It was not possible to prevent the formation of a large amount of oxyiodide in this treatment.
2. The reaction of Y_2O_3 with I_2 in molten ammonium thiocyanate. The product did not appear to contain a significant amount of YI_3 .
3. The iodination of a Y_2O_3 -carbon mixture at $1300^\circ C$. This was a difficult reaction to carry out and the product did not approach pure YI_3 .

As yttrium iodide was of possible use in the preparation of yttrium metal by the thermal decomposition of this salt, some of its physical properties pertinent to such a use were examined. The vapor pressure of the salt was measured over the region 10^{-2} mm to 10^{-4} mm using a quartz fiber microbalance adaptation of the Knudsen method; a vapor pressure equation was obtained,

$$\log P_{mm} = \frac{-11706(\pm 337)}{T} + 9.54 (\pm 0.38) ,$$

which indicated a heat of sublimation of 53.6 ± 1.5 Kcal/mole in the temperature region studied. Of primary interest was the temperature

at which the iodide would decompose on a hot wire. This was studied by subliming a measured quantity of the salt onto a hot filament and measuring the quantity of metal deposited and the amount of iodine liberated. A negligible degree (less than 5%) of decomposition of YI_3 was observed up to $1600^\circ C$, whereas experiments with ZrI_4 in the same apparatus indicated a high degree of decomposition under similar conditions, in agreement with published information on ZrI_4 . This study indicated that the thermal decomposition of YI_3 was not likely to be a convenient method of preparing the metal.

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3. Preparation of Yttrium Metal

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Two general methods for preparing yttrium metal were investigated extensively. One method involves the high temperature reduction of yttrium fluoride with calcium carried out above the melting point of yttrium metal (1510°C) in a tantalum crucible. The second method employs the formation of a low melting yttrium magnesium alloy and eutectic slag mixture enabling the reaction to be carried out at 1000°C in a titanium or zirconium crucible.

3.1 Preparation of Yttrium in Tantalum Crucibles

The first preparation of yttrium in this laboratory was by the reduction of yttrium fluoride with calcium.¹ This reaction was carried out at 1575°C in an argon atmosphere on a 5 to 50 gram scale using tantalum crucibles. After vacuum remelting, the yttrium ingot was obtained by peeling away the tantalum crucible. To scale up the preparation of yttrium by this reaction, a series of modifications in the furnace design and operating techniques were devised on a 300 to 1000 gram scale, as will be described in this section. The details of

the evolved process using this technique on the large scale will be described in the next section of this report.

The direct reduction of yttrium fluoride with calcium in tantalum crucibles was scaled up to prepare 200 grams of metal per reduction, using crucibles 2 1/2" in diameter by 6" high. These were destroyed to recover the yttrium; however, since the molten products occupied only one third of the volume of the crucibles, this represented very inefficient use of the tantalum. An obvious move to improve the economics of this process was to add more reactants to the crucible at the reaction temperature and thus fill it with molten products. This modification was accomplished by placing the mixed charge in a hopper on top of the furnace as shown in Fig. 2. The hopper and furnace were connected so as always to contain the same atmosphere. In addition, the hopper was equipped with a stopper-rod assembly so that the charge could be added after the furnace was vacuum out-gassed and filled with argon. After the reaction crucible was filled with charge and heated to obtain molten products, more charge was added and melted to fill the crucible. To obtain the yttrium metal, the tantalum was again peeled away from the ingot after vacuum melting.

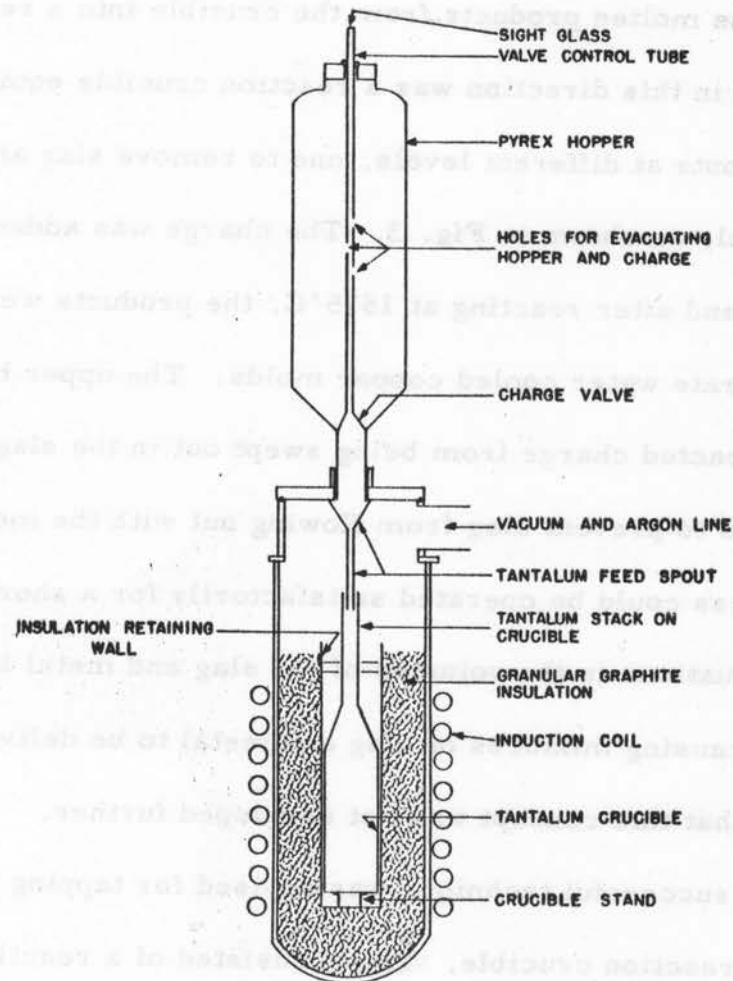


Fig. 2. Furnace and Hopper Assembly Employed in Reductions in Tantalum Crucibles.

To obtain still greater use of the tantalum crucibles, a technique was sought to tap the molten products from the crucible into a reuseable mold. One attempt in this direction was a reaction crucible equipped with two tapping spouts at different levels, one to remove slag and one to remove metal, as shown in Fig. 3. The charge was added in the usual manner, and after reacting at 1575°C , the products were delivered into separate water cooled copper molds. The upper baffle was to prevent unreacted charge from being swept out in the slag, and the lower baffle was to prevent slag from flowing out with the metal. Although this process could be operated satisfactorily for a short time, random fluctuations in the volumes of the slag and metal layers always occurred, causing mixtures of slag and metal to be delivered to both molds, so that this concept was not developed further.

Another more successful technique was devised for tapping the products from the reaction crucible. This consisted of a reaction crucible and hopper assembly as previously described, but with a small open tantalum pipe leading from the bottom of the reaction chamber. This pipe extended out into a cooler region of the furnace so that the first yttrium that formed drained into it and froze, sealing the spout. After the reaction chamber was filled to about three fourths of its capacity with liquid reaction products, the pipe was heated to melt

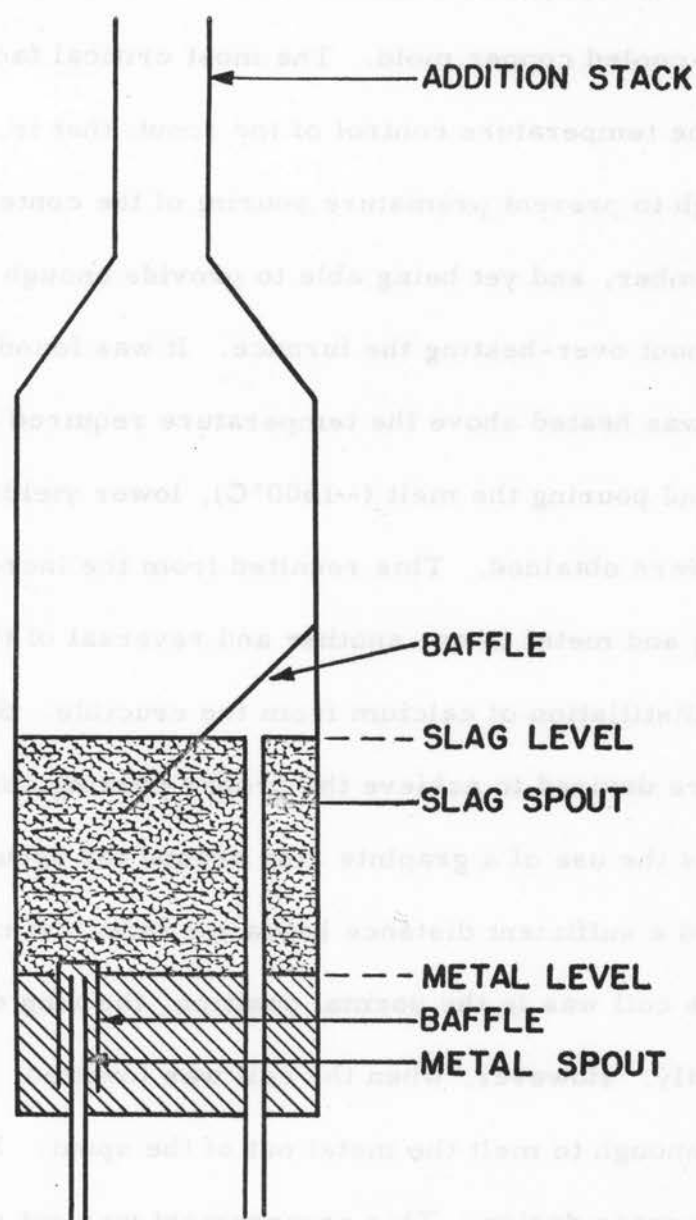


Fig. 3. Reaction Crucible with Tapping Spouts for Removing Slag and Metal Phases.

out the plug, and the yttrium metal, followed by the slag, drained into a water-cooled copper mold. The most critical factor in this process is the temperature control of the spout; that is, keeping it cool enough to prevent premature pouring of the contents of the reaction chamber, and yet being able to provide enough heat to tap the melt without over-heating the furnace. It was found that as the furnace was heated above the temperature required for reacting the charge and pouring the melt ($\sim 1600^{\circ}\text{C}$), lower yields of less pure metal were obtained. This resulted from the increased solubility of slag and metal in one another and reversal of the reduction reaction by distillation of calcium from the crucible. Several schemes were devised to achieve the proper pouring conditions. The first was the use of a graphite ring around the spout. This ring extended a sufficient distance below the induction coil so that when the coil was in the normal position, the ring did not heat efficiently. However, when the coil was lowered, the ring became hot enough to melt the metal out of the spout. Figure 4 shows this furnace design. This arrangement was not completely satisfactory as some overheating of the furnace occurred in the pouring process and, furthermore, only fair quality metal was obtained.

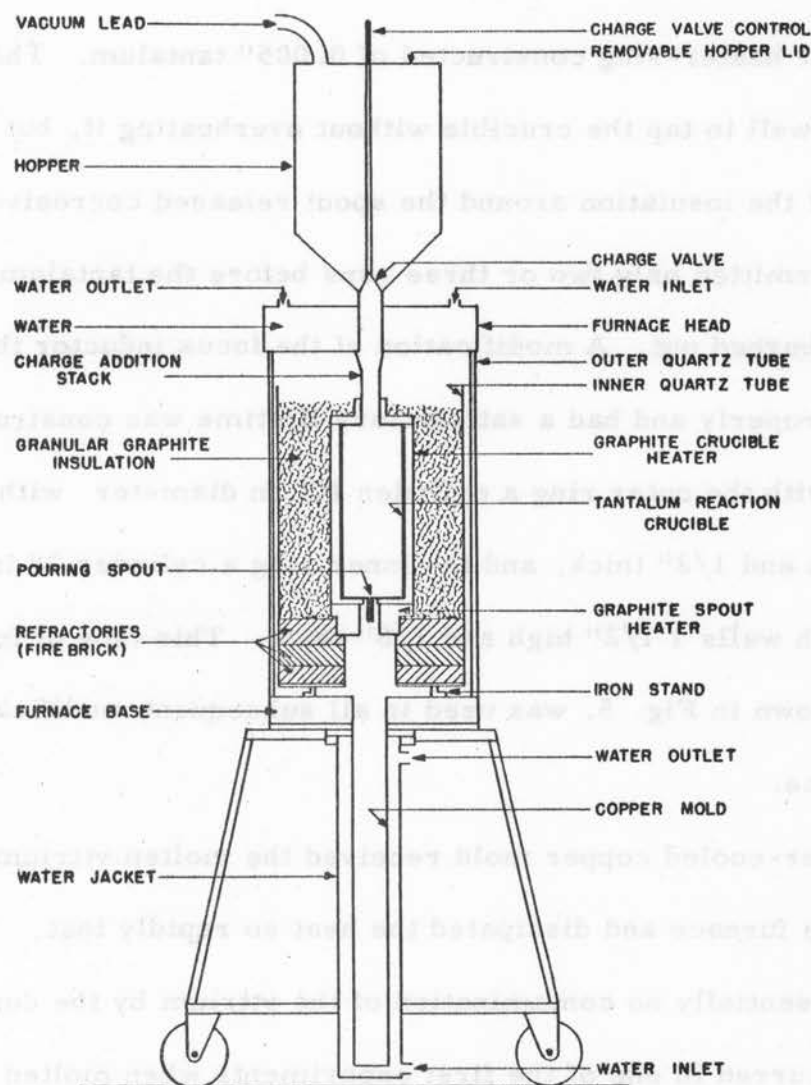


Fig. 4. Complete Furnace Assembly for Reduction and Pouring of Yttrium.

A second technique devised for concentrating heat on the spout was the use of a focus inductor, a split, outer pick-up ring of titanium 10" in diameter and $1/16$ " in thickness, concentric with a 2" diameter heater-ring constructed of 0.005" tantalum. This served very well to tap the crucible without overheating it, but the outgassing of the insulation around the spout released corrosive gases and permitted only two or three runs before the tantalum heater-ring burned out. A modification of the focus inductor that performed properly and had a satisfactory lifetime was constructed of graphite with the outer ring a cylinder 10" in diameter, with walls 4" high and $1/2$ " thick, and the inner ring a cylinder 2" in diameter with walls $1\ 1/2$ " high and $1/8$ " thick. This type of focus inductor, shown in Fig. 5, was used in all subsequent modifications of this furnace.

The water-cooled copper mold received the molten yttrium and slag from the furnace and dissipated the heat so rapidly that there was essentially no contamination of the yttrium by the copper. A failure occurred in one of the first experiments when molten yttrium alloyed with and melted through the bottom of the copper mold where a slight convexity caused an air bubble to form in the water jacket, and prevented efficient removal of heat from this

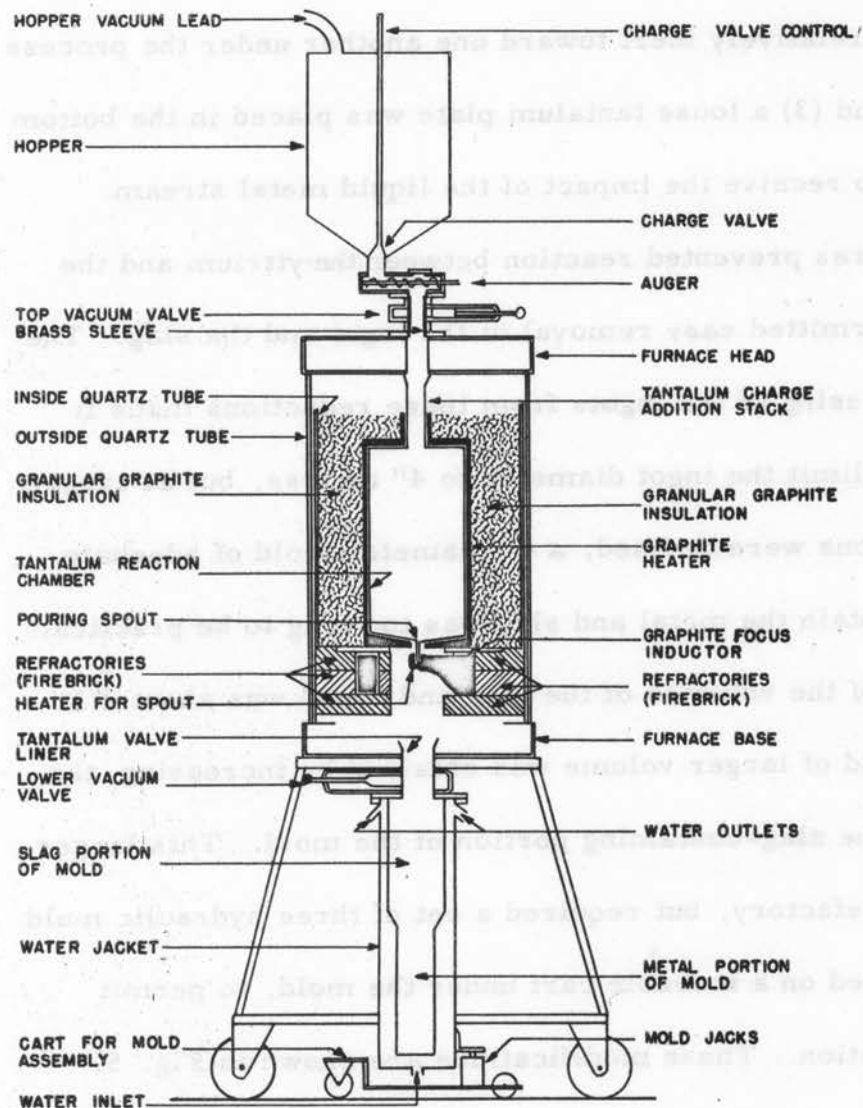


Fig. 5. Improved Design of Reduction and Pouring Furnace with Graphite Focus Inductor.

spot. Three steps were taken to assure that this did not recur:

(1) the water inlet was redesigned so that the incoming water was directed onto the bottom of the mold; (2) the mold was chromium plated, as studies of yttrium-chromium alloys indicated these metals to be relatively inert toward one another under the process conditions; and (3) a loose tantalum plate was placed in the bottom of the mold to receive the impact of the liquid metal stream.

These measures prevented reaction between the yttrium and the mold, and permitted easy removal of the ingot and the slag. The further processing of the ingots from these reductions made it necessary to limit the ingot diameter to 4" or less, but as larger scale operations were devised, a 4" diameter mold of adequate volume to contain the metal and slag was too long to be practical. As the ratio of the volumes of the slag and metal was about 2:1, a shorter mold of larger volume was obtained by increasing the diameter of the slag-containing portion of the mold. This larger mold was satisfactory, but required a set of three hydraulic mold jacks, arranged on a movable cart under the mold, to permit easy manipulation. These modifications are shown in Fig. 5.

As the size of the reaction crucible was increased in the scale-up of the process, a larger stainless steel hopper was employed. However, it was found that the stopper rod assembly for dropping the charge into the reaction chamber did not permit precise control of the rate of addition of the charge, for bridging would occur in the hopper or the charge addition stack. When this occurred, the material either could not be discharged, or would suddenly break through, resulting in too much material in the reaction chamber. To correct this, the hopper was modified by adding a screw feeding mechanism, shown in Fig. 5. The auger was driven by a variable-speed motor so that the addition rate could be carefully controlled.

A further modification of the furnace was the addition of two slide-type vacuum valves, shown in Fig. 5, which reduced the waiting time between runs by eliminating the cooling period. The upper valve, 2" in diameter, obtained from Vacuum Research Corporation, permitted direct discharge of the reactants from the auger feed into the addition stack. To prevent the charge material from entering the mechanism of the valve, a sleeve was placed in the valve body; a rack and pinion was used to insert or retract the sleeve. This permitted sealing off the reaction chamber

from the hopper while the latter was being recharged, evacuated, and refilled with argon gas in preparation for another run.

In like manner, a 4" diameter valve, shown in Fig. 6, obtained from Consolidated Vacuum Company, was installed just below the furnace so that the filled mold could be removed. Another mold could then be attached, evacuated and filled with argon, ready to receive another melt. Because of occasional pours that spewed off to one side, it was necessary to line the retractable sleeve of this valve with tantalum, as shown in Fig. 6, to prevent damage to the valve and contamination of the yttrium in such cases. The vacuum connection for evacuating the mold was located just below the valve.

As the hot metal entered the cold mold, the argon gas in the mold expanded rapidly, developing a sudden pressure rise. This was remedied by the use of a special valve, connected to the lower part of the furnace. This valve consisted of a 2" diameter, smooth brass disk that rested freely on an "O" ring seated in a flange. The weight of the brass disk was such that a small pressure rise in the furnace would lift the plate and bleed off the gas.

Temperatures were measured by two tungsten-niobium thermocouples, one located in the wall of the graphite heater several

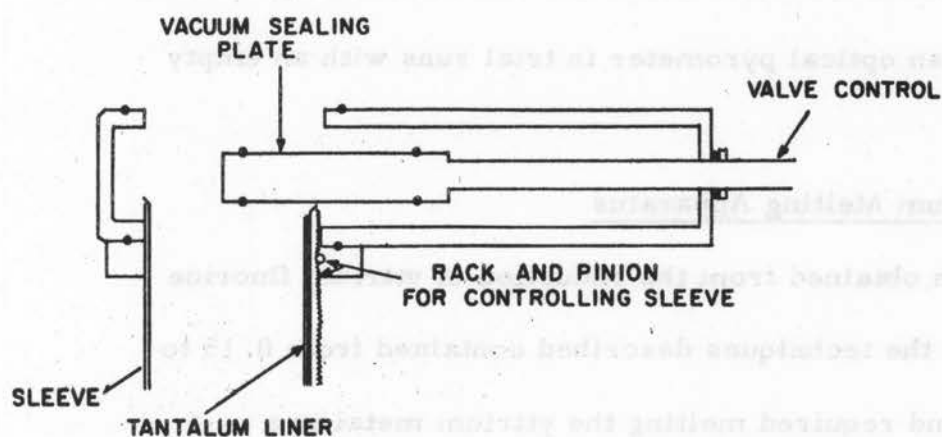


Fig. 6. Valve Assembly with Tantalum-Lined Retractable Sleeve.

inches from the bottom, and the other in the focus inductor to indicate the spout temperature. In spite of the inaccuracy of these thermocouples and the frequent replacements required, they were the most suitable temperature indicators available. An optical pyrometer was not satisfactory because of the vapors released by the charge inside the furnace. However, the thermocouples were calibrated with an optical pyrometer in trial runs with an empty furnace.

3.1.1 Vacuum Melting Apparatus

The yttrium obtained from the reduction of yttrium fluoride with calcium by the techniques described contained from 0.15 to 0.5% calcium and required melting the yttrium metal in a vacuum to eliminate this impurity. The calcium was readily removed by such a melting operation because of its high vapor pressure at the melting point of yttrium metal (1550°C). The rapid distillation of the calcium out of the molten yttrium often ejected a considerable quantity of yttrium from the crucible, even when the yttrium was first melted in an inert atmosphere, prior to the slow evacuation of the furnace. A drip melting procedure was

devised in which the yttrium was melted in a crucible containing baffles, as shown in Fig. 7. As the yttrium flowed over the baffles in a thin stream, the calcium distilled away slowly and the yttrium collected in the mold in the form of a rough-surfaced ingot with deep cold shuts. The metal thus obtained was ~~are melted to form a~~ smooth ingot.

3.1.3 Preparation of Low Oxygen Content Metal in Tantalum Crucibles

The metal obtained from the reduction of yttrium fluoride with calcium was found to contain 1400 to 2000 ppm oxygen, and an attempt was made to lower the oxygen content by various modifications of the reduction technique. Also, the oxygen content of the yttrium fluoride was lowered by various techniques so that a better quality reactant was obtained.

Calcium picks up oxygen from the air during mixing and loading operations, even after it has been redistilled under vacuum and ground and stored under an argon atmosphere. Therefore, the calcium was vacuum distilled directly into the reduction crucible and melted into a solid ingot under an inert atmosphere. The best grade of vacuum-melted yttrium fluoride was added to

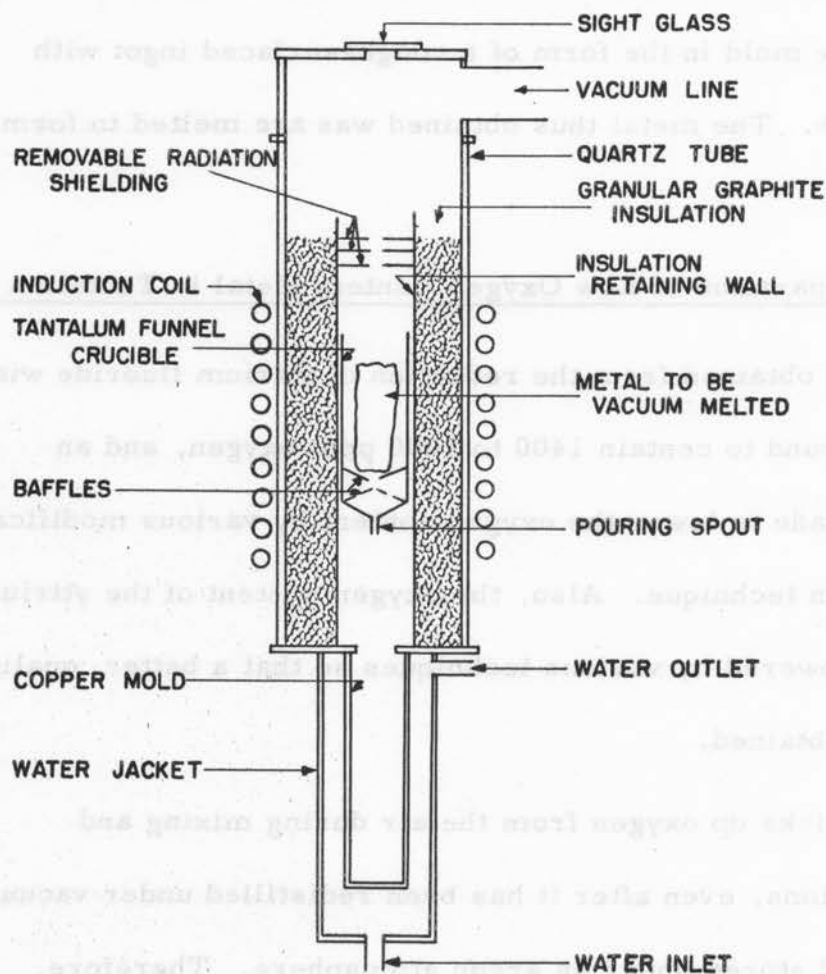


Fig. 7. Assembly Used for Drip Melting Yttrium into Water Cooled Copper Mold.

this crucible and reacted with the calcium at 1600°C in a purified argon atmosphere. Yttrium metal was obtained on a 100 gram scale and was found, by spectrographic analysis, to contain from 490 to 670 ppm oxygen after vacuum melting. Several experiments were carried out on a 30 - 100 gram scale in which vacuum-melted yttrium fluoride was placed in an open tantalum crucible. This crucible was suspended in another tantalum crucible which contained an ingot of vacuum-distilled calcium that had been melted in an inert atmosphere. The outer tantalum crucible was sealed in a vacuum and heated to about 1600°C for 5 hours. The calcium vaporized and reacted with the fluoride to yield metal containing 540 ppm oxygen. Since the calcium entering into this reaction came from the vapor state, it probably contributed a negligible amount of oxygen to the product, which suggests that a better grade of fluoride is required to prepare yttrium containing less than 500 ppm oxygen by this method.

Substitution of lithium for calcium in some reduction experiments did not appear to lower the oxygen content of the yttrium metal produced, but did make operations more convenient in one respect

in that a lower melting slag was formed. However, the added precautions necessary to handle lithium made its use inadvisable for routine production of metal unless more definite improvements in purity of the final product were apparent.

3.2 Yttrium-Magnesium Intermediate Alloy Process

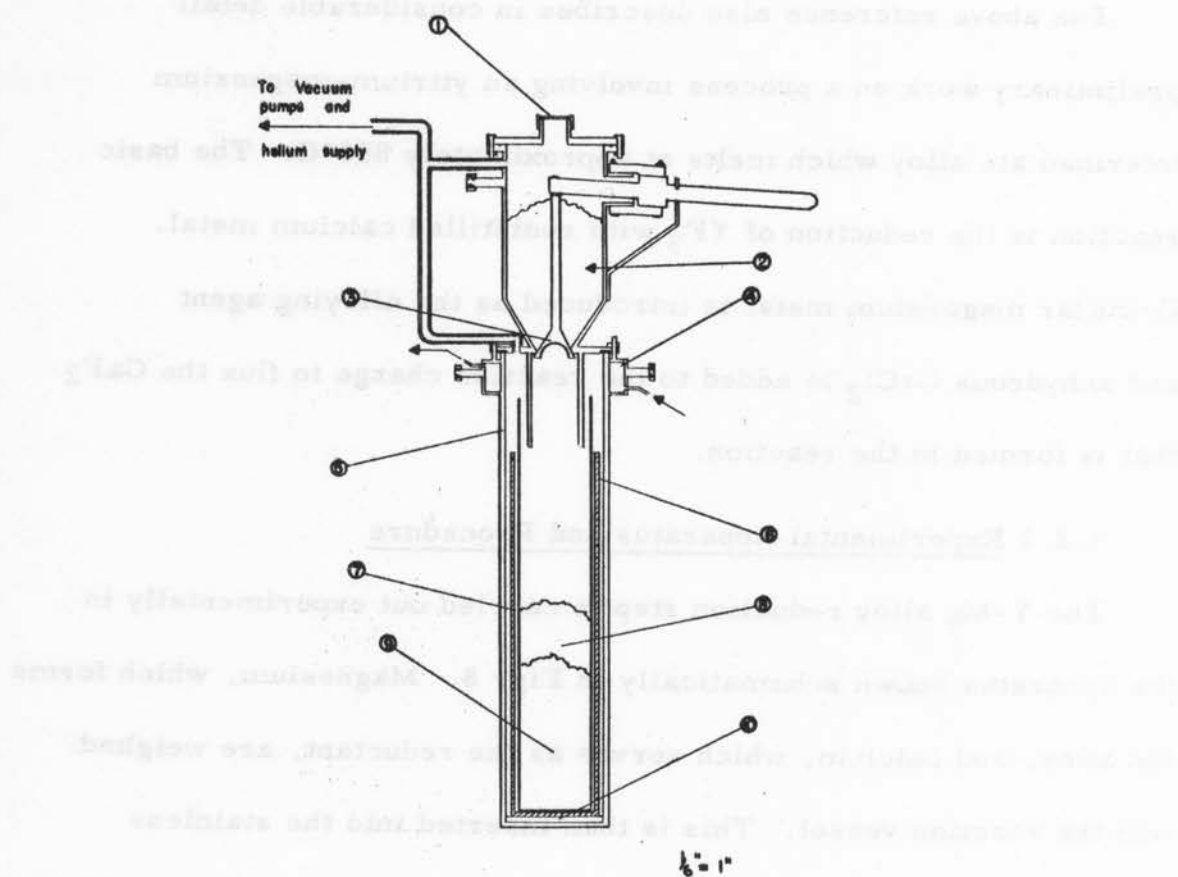
The relatively high melting point and reactivity of yttrium introduces serious limitations on the reaction vessels in which yttrium metal can be prepared. Formation of a low melting intermediate alloy of yttrium with one of the common volatile metals offers the possibility of a lower reaction temperature. By this technique it might be possible to use something besides the very high melting refractory materials as reaction vessels for the reduction process.

Carlson, Schmidt and Spedding² described the preparation of yttrium metal by a zinc intermediate alloy process in which YF_3 and ZnF_2 were co-reduced by calcium in a sealed iron vessel lined with calcium fluoride. The zinc was subsequently sublimed off and yielded yttrium sponge metal.

The above reference also describes in considerable detail preliminary work on a process involving an yttrium-magnesium intermediate alloy which melts at approximately 850°C. The basic reaction is the reduction of YF_3 with redistilled calcium metal. Granular magnesium metal is introduced as the alloying agent and anhydrous CaCl_2 is added to the reaction charge to flux the CaF_2 that is formed in the reaction.

3.2.1 Experimental Apparatus and Procedure

The Y-Mg alloy reduction step is carried out experimentally in the apparatus shown schematically in Fig. 8. Magnesium, which forms the alloy, and calcium, which serves as the reductant, are weighed into the reaction vessel. This is then inserted into the stainless steel retort. A mixture of anhydrous CaCl_2 and YF_3 are loaded into the hopper and the entire assembly is evacuated and back-filled with helium or argon gas. The commercial anhydrous CaCl_2 is given a final dehydration by heating to 450°C under a dynamic vacuum prior to the reduction step. The magnesium and calcium are heated in the reaction vessel to approximately 950°C at which temperature they form a homogeneous melt. The CaCl_2 - YF_3 powder mixture is then added from the hopper into the hot zone of the reaction vessel. Heating of the retort and its



- | | |
|--|----------------------|
| 1. Sight window | 6. Graphite liner |
| 2. Hopper containing YF_3 and CaCl_2 | 7. Ti or Zr crucible |
| 3. Feed valve with operating handle | 8. Magnesium metal |
| 4. Water jacket | 9. Calcium metal |
| 5. Stainless steel retort | 10. Graphite disc |

Fig. 8. Schematic Drawing of Assembled Reduction Retort and Hopper.

contents is carried out in a gas fired furnace to a maximum temperature of 975-1000°C. At the conclusion of the reaction, the molten alloy phase containing between 20 and 25 w/o magnesium segregates to the bottom and the immiscible slag phase of CaF_2 + 50% CaCl_2 floats to the top.

In order to facilitate removal of the slag and especially of the alloy, the retort is raised from the furnace and placed in a tilting rack where the fluid products solidify in a reclining position. In this way the solid products can readily be removed physically from the container without damage to the vessel. Figure 9 is a photograph of the retort after it has been removed from the furnace and as it rests in the tilting position.

The metals zirconium, titanium, and tantalum, have been used successfully as the material for the reaction vessel. Amounts of 0.5 - 1.0 w/o Zr, 0.1 - 0.2 w/o Ti and less than 0.01 w/o Ta are introduced into the yttrium metal by the respective container materials.

The resulting alloy, which contains approximately 24 w/o Mg and 3 w/o Ca, is hard and brittle and retains its bright metallic lustre for prolonged periods in dry air. The alloy is crushed in a conventional jaw crusher into pieces 1/2 inch in diameter. The magnesium and calcium are removed by heating the alloy slowly to a temperature of 1000°C to 1200°C in vacuo. The alloy is contained in a titanium vessel during this operation, and the magnesium vapors are collected on an air cooled condenser. The

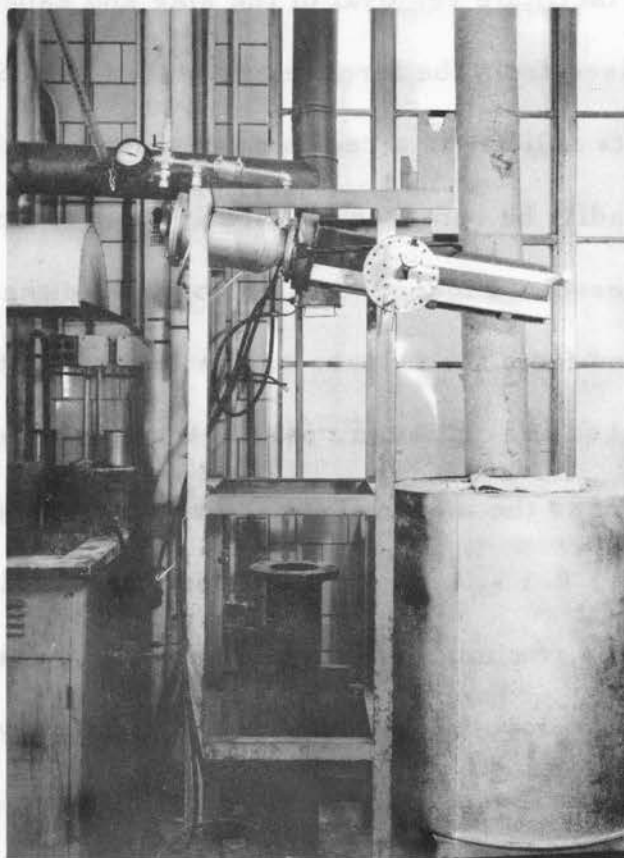


Fig. 9. Photograph of Retort in Reclining Position upon Completion of Reduction.

resulting yttrium metal is a bright porous sponge which can be consolidated by compacting into electrodes and consumable-arc-melting into an ingot. The details of the "demagging" and arc-melting steps are presented in the next section of this report. Likewise, many of the research and development results which are described in this chapter were obtained from routine reduction or large scale experiments which were carried out in the enlarged equipment described in detail in the next section of this report.

A typical analysis of the yttrium metal prepared during 1957 by the magnesium alloy process is given in Table V. This metal was prepared from granular calcium and magnesium and from fluoride, the intensity ratio of which was less than 0.50. The reductions were carried out in a zirconium pot which accounts for the high zirconium values. The relatively high nickel values are attributed to pick up from the inconel tube during the hydrofluorination step.

Results on a study of the metallography of yttrium has been described in detail in a recent paper by Carlson, Eash and Spedding.³ A typical microstructure of yttrium is reproduced in Fig. 10 which shows the as-polished structure of arc-cast metal. The dark stringers within the grains have been identified as Y_2O_3 . The development of a

Table V

Typical Analysis of Yttrium Prepared
by Magnesium Alloy Process in 1957

Element	w/o
Calcium	0.001
Carbon	0.020
Iron	0.015
Magnesium	0.003
Nickel	0.035
Nitrogen	0.015
Oxygen	0.20-0.40
Titanium	0.005
Zirconium	0.5 - 0.8

satisfactory chemical etchant for yttrium has been rather slow due primarily to a tendency of the metal to form a film with most chemical reagents. The most satisfactory etchant that has been developed to date is a methyl alcohol-3% HNO_3 solution that is applied to the specimen by immersion. The microstructure of an yttrium specimen containing 1020 ppm oxygen is shown in Fig. 11 as it appears upon etching with this solution.

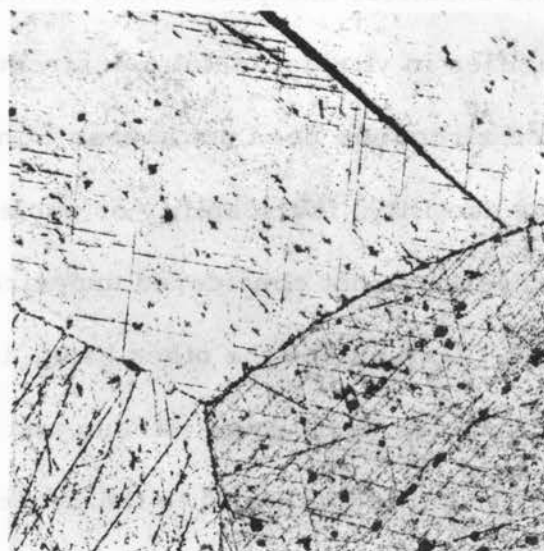


Fig. 10. Photomicrograph of Yttrium Containing 3000 ppm O_2 .
Etchant: 3% HNO_3 - CH_3OH solution. 250X.

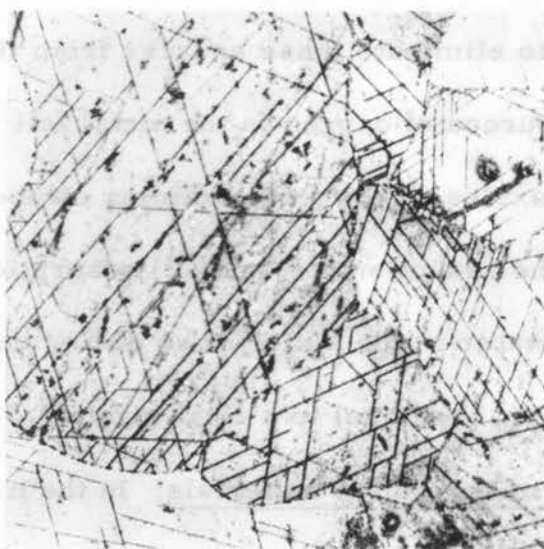


Fig. 11. Photomicrograph of Yttrium Metal Containing 1020
ppm O_2 . Etchant: 3% HNO_3 - CH_3OH solution. 250X.

3.2.2 Experiments on Improving the Purity of Yttrium Metal

As is evident from the chemical analyses shown in the preceding table, the principal impurities in yttrium metal are zirconium, oxygen and possibly nickel. Since zirconium does not appear to have a deleterious effect upon the ductility, fabricability or nuclear cross-section of yttrium, its presence is not considered undesirable, at least for most applications. Oxygen, on the other hand, is believed to have an adverse effect upon the ductility of yttrium and the poor cold working property of yttrium is attributed to the presence of this impurity. The effect of the amount of nickel reported is not known although there are some indications that it may be undesirably high also.

An intensive investigation was undertaken to find the sources of oxygen in the metal and to eliminate these sources from the process. Broadly speaking, the sources of oxygen in the metal fall into two categories; (1) residual oxides or oxygen-containing compounds in the ingredients used in the reduction step and (2) adsorption of, or reaction with oxygen or water in the atmosphere during handling of the materials in processing the metal to a final ingot.

Oxygen contribution of ingredient materials: In the magnesium alloy process described above, all of the ingredients, YF_3 , Ca, Mg

and CaCl_2 , are potential contributors of oxygen. All of them, with the possible exception of Mg, were found to contribute significant amounts of oxygen. The amount of oxygen contributed by the fluoride was unknown at the time most of this work was done, since no direct quantitative determination of the oxygen content of the fluoride had been devised at that time. It has been demonstrated experimentally, however, that oxygen present in the fluoride, either as Y_2O_3 , or YOF is transferred almost quantitatively into the metallic phase during the reduction step. In an effort to arrive at some estimate of the amount of oxygen that is added by the fluoride, an attempt was made to correlate oxygen content of the yttrium with the oxygen intensity ratio of the fluoride from which it was prepared. A total of 30 reductions were made employing fluoride with an intensity ratio in the range of 0.25-0.35, 42 reductions with 0.35 to 0.45 fluoride, and 14 reductions were made employing fluoride in the range of 0.45 to 0.50. Although the oxygen content of the resulting metal varied considerably for each range of fluoride, an average value was determined for each. The 30 yttrium ingots prepared from the lower range of fluoride contained an average of 1675 ppm O_2 with a standard deviation from the mean of ± 60 ppm. The 42 ingots prepared from fluoride of the next higher range contained an average of 1685 ± 60 ppm O_2 . These data show

that there is little difference in the quality of the fluoride with intensity ratios in the range of 0.25 to 0.45. The average oxygen content of the 14 ingots prepared from the 0.45 to 0.50 OIR fluoride was about 600 ppm O_2 higher than for the intermediate range material, and the slag-metal separation during the reduction step was generally poor. For these reasons, a maximum intensity ratio of 0.45 was set for acceptable production grade fluoride. These data do not give any indication, however, as to the residual oxygen content of the fluoride.

The second potential source of oxygen is calcium metal, particularly when used in granular form. A chemical analysis was performed on some calcium metal employing a mercury amalgam technique. The results of the analyses are presented in Table VI.

Table VI

Oxygen Content of Calcium Metal

Form of Calcium	ppm O_2
1. Massive; freshly redistilled	approx. 300
2. Granular; distilled and ground in dry room; by Ames Lab.	approx. 1000
3. Granular; redistilled and ground by Nelco	approx. 1500

A comparison was made between yttrium metal prepared with granular calcium and with massive calcium on the small experimental scale. All other ingredients were identical in the reduction, and the demagging, and melting operations were carried out simultaneously on comparative samples. Duplicate runs were made. As can be seen from the data presented in Table VII, the oxygen content of the yttrium that was prepared with massive calcium is approximately 1000 ppm below that prepared with the granular calcium.

Table VII

Oxygen Content of Yttrium Metal

Prepared with Different Forms of Calcium

Ca Form	ppm O ₂	
	Run 1	Run 2
Redistilled granular calcium	2800	2700
Redistilled massive calcium	1700	1930
Δ oxygen	1100	770

In the large scale development work, 21 reductions were made with granular calcium employing fluoride of 0.35 to 0.45 intensity ratio. It is interesting to note that the average oxygen content of the resulting ingots

was 2575 ± 75 ppm. A series of 29 reductions employing massive calcium and a similar grade of yttrium fluoride showed an average of 1725 ± 50 ppm O_2 in the ingot metal, a difference of 850 ppm O_2 .

Finally, an investigation was made on the amount of oxygen that is contributed by the $CaCl_2$. Anhydrous C. P. grade $CaCl_2$ obtained from Baker Chemical was used in the series of experiments. As mentioned previously, this material contains a small amount of residual water as it is received. Some of this chloride was dried by heating in vacuo at $450^\circ C$ for 10 hours, a procedure followed in the experiments described in the preceding pages. A second batch was dried by heating at $450^\circ C$ for 5 hours in an HCl atmosphere. A third batch was first vacuum dried and then heated in HCl at $450^\circ C$ for 5 hours. A series of reductions was then run in which all the other ingredients were the same and identical conditions were maintained. Duplicate runs were made for each of these drying conditions. The data presented in Table VIII indicate that significant and perhaps variable amounts of oxygen are introduced by the $CaCl_2$ that has merely been vacuum dried. Since these experimental results were obtained with the small (3 pound) reduction equipment, an attempt was made to duplicate the results on the large (100 pound) scale, but no significant improvement in the metal quality was obtained on the large scale by drying the $CaCl_2$ in an HCl

atmosphere. This is believed to have been due to inadequate facilities for treating large quantities of CaCl_2 with HCl gas, however.

Table VIII
Experiments in Drying of CaCl_2

Drying conditions	ppm O_2 in Final Y Metal
Vacuum dried CaCl_2	1920 2460
HCl over Comm'l CaCl_2	1430 1670
HCl over vacuum-dried CaCl_2	1300 1375

Oxygen pickup during processing: The other major source of oxygen is postulated to be from absorption of, or reaction with oxygen or atmospheric moisture, by the materials during one of the processing steps. Since most crushing and transfer operations had been made in air, experiments were carried out to determine the reactivity of the alloy and of the sponge toward the atmosphere. Uniform batches of alloy and sponge were exposed to normal winter atmospheric conditions (room temperature 28°C , relative humidity about 30%). Other samples were exposed to a highly humid atmosphere (about 90% relative humidity). While the results were

somewhat inconclusive, one observation was readily apparent. The alloy is highly reactive toward a humid atmosphere, but does not appear to pick up oxygen when exposed to a low-humidity atmosphere for as long as 5 days. On the other hand no significant increase in oxygen content was observed in the sponge in either type of atmosphere, even after an exposure of 5 days in a highly humid atmosphere. These observations emphasize the importance of maintaining a dry atmosphere on the alloy during the crushing and screening operations, particularly during the humid seasons of the year. Air tight enclosures have been constructed around one of the jaw crushers and around the screening equipment.

The oxygen pick-up during the arc melting step was likewise investigated. Since direct oxygen analysis on the sponge cannot be carried out by present methods the following procedure was followed. A sample was taken from the first melt, four-inch-diameter ingot and another sample was taken from the six-inch-diameter ingot obtained on the second melting step. A comparison of oxygen values for ten such sample pairs revealed an average increase of approximately 100 ppm oxygen due to the vacuum arc melting operation.

A similar series of experiments was run to determine the oxygen pick-up during the "demagging" step. Several batches of sponge were

run through a second heating cycle identical to the first "demagging" run and the oxygen content of the metal was determined before and after the second heating treatment. The samples to be compared were then arc melted into small ingots from which analytical specimens were taken. On the basis of six such experiments an increase of approximately 500 ppm O_2 was observed. Because the results were erratic and therefore not conclusive they are now being verified by repeated experiments.

Decrease in metallic impurities: Although the presence of zirconium in the amount of 0.5 to 0.8 w/o does not appear to have an adverse effect upon the mechanical or nuclear properties of yttrium, it does nevertheless represent a rather extensive amount of alloying. For this reason several reductions were carried out in a titanium reaction vessel. Thirty ingots that were prepared employing crucibles for both the reduction and "demagging" steps contained an average of $0.15 \text{ w/o Ti} \pm .02 \text{ w/o}$. This amount of titanium does not appear to have a deleterious effect upon the mechanical properties of yttrium metal nor does it raise the nuclear cross-section of yttrium to a measurable extent.

A further advantage in using a titanium reduction pot is

that the initial cost of the titanium plate from which the pot is fabricated is considerably lower than for zirconium. Furthermore, the expected lifetime of such a pot is much longer than for the identical size zirconium pot due to the slower dissolution rate. For instance, one titanium pot (1/4" wall thickness) was used for a total of 38 reductions before it failed, whereas the maximum number of runs in a similar sized zirconium pot was found to be approximately 20.

Two experimental reductions were carried out in a tantalum pot in an effort to prepare a few pounds of yttrium metal that was low in all metallic impurities. The metal prepared in this manner contained less than 0.01 w/o Ta, which is the lower limit of detection for that element by present spectrographic methods. The tantalum content of the metal is believed to be well below that figure.

Since there is no specific knowledge as to the level at which some of the metallic impurities can be tolerated, it is planned to study the effect of small amounts of titanium, tantalum, nickel, zirconium, magnesium and possibly others upon the tensile strength and ductility of yttrium metal. A new Tinius-Olson screw-type tensile machine has recently been purchased by the Laboratory and the preparation of alloys for use in preparing tensile specimens is now in progress.

3.2.3 Modifications in Y-Mg Alloy Process

Because CaCl_2 was found to add a significant amount of oxygen to yttrium metal, several modifications in the process were considered to eliminate this source of oxygen. The substitution of CaI_2 for CaCl_2 (by the addition of I_2 and excess Ca to the charge) proved unsatisfactory primarily because of an unfavorable density relation between the slag and the alloy. Likewise, LiCl was tried as the fluxing agent but the resulting yttrium was of poorer quality than that obtained by the use of CaCl_2 . Another modification that was considered was the substitution of YCl_3 for YF_3 in total or in part. This would eliminate CaCl_2 as one of the ingredients in the charge because the reaction with calcium would yield the CaCl_2 required to flux the slag. However, because of the difficulties encountered in preparing high purity anhydrous YCl_3 , no experiments have been tried to date on the reduction of this yttrium compound.

Lithium as the reductant: A method that seemed more promising was the substitution of lithium for calcium as the reductant. Since the melting point of LiF , which is formed in the reaction, is 870°C (compared with 1330°C for CaF_2) no flux is required for the slag under the temperature conditions at which the magnesium intermediate alloy process is normally carried out. A series of small scale

reductions was run in which YF_3 , massive lithium and magnesium were placed in the titanium vessel and reacted together at $975^\circ C$. The resulting Y-Mg alloy was less brittle and somewhat more pyrophoric than that obtained by the use of the calcium reductant. However, with proper precautions this alloy could be crushed and "demagged" by the usual techniques. In duplicate reductions, lithium was added to the charge in the ingot form as it was received from the commercial supplier. In two other experiments, the lithium was filtered through a sintered steel porous plate prior to the reduction step. In another pair of reductions, the lithium was vacuum distilled, condensed and allowed to drip into the titanium reaction vessel. The reduction was then carried out in the manner described above. The lithium in the as-received condition apparently contains considerable amounts of oxygen and nitrogen which are transferred to the yttrium. This can be inferred from the data presented in Table IX. While the data are somewhat erratic, both filtering and distillation of the lithium appear to remove nitrogen and at least a portion of the oxygen.

Calcium-lithium as co-reductants: Since lithium is expensive and also quite reactive, a series of experiments were run in which calcium and lithium were employed as co-reductants. The products

Table IX

Yttrium Metal Prepared by Reduction of YF_3 with Li

Condition of Lithium	Analysis of Yttrium Metal	
	ppm O_2	ppm N_2
1. As received; surface cleaned	2250	830
" " " "	3200	960
2. Filtered lithium	1575	210
" "	1200	180
3. Distilled lithium	1575	200
" "	950	100

from such a combination are CaF_2 and LiF which form a low melting salt mixture. Thus, by the use of a small quantity of lithium metal it is possible to eliminate the CaCl_2 entirely from the process. A preliminary series of reductions was run in which the ratio of the Ca:Li reductants was varied over a wide range; 44 w/o, 34 w/o, 26 w/o, 22 w/o, 18.5 w/o and 15 w/o Li in Ca were tried. The reaction proceeded satisfactorily for all but the lowest lithium ratio, but the most satisfactory results were obtained with a composition of 22 w/o Li and a combined excess of calcium and lithium of 10% over the stoichiometric amounts required.

A number of 100-pound reductions were carried out in the large reduction equipment employing the 22 w/o Li - 78 w/o calcium reduction charge. This was accomplished in the following manner using the existing large scale reduction equipment. Massive calcium and magnesium were placed in the titanium reaction vessel. The lithium was filtered in vacuo through a mat of steel wool and collected in a semicircular iron bucket. After the filtered lithium had solidified, the bucket was suspended in an inverted position from the lid of the charged retort. The lithium (m. p. 180°C) melted and dripped into the calcium and magnesium during the initial part of the heating operation. When the Ca-Li-Mg mixture reached a temperature of 950°C the YF_3 was admitted from the hopper into the reaction vessel. Considerable difficulty was encountered in these reductions by the tendency of a low density phase to form and float on the surface of the slag. This phase was rich in lithium and magnesium but contained some yttrium as well. Efforts to eliminate this difficulty have not been entirely successful.

The Y-Mg alloy from the large scale experiments was processed in the usual manner and melted into 6" diameter ingots. Oxygen analyses were made on the metal prepared in this way. These results are presented in Table X. The average oxygen content of the 14 ingots

Table X

**O₂ & N₂ Content of Yttrium Metal Prepared by Calcium-
Lithium Co-reduction Method**

Ingot No.	ppm O ₂	ppm N ₂
C-246	1160	185
C-255	1125	285
C-259	1280	155
C-261	1360	165
C-265	1000	60
C-267	1050	290
C-271	1300	175
C-272	1570	175
C-284	1270	160
C-288	1700	155
C-299	1710	---
C-302	1390	150
C-307	2120	85
C-308	1830	150

is 1400 ppm O_2 , with a standard deviation from the mean of ± 75 ppm.

When this is compared with a mean of 1675 ± 50 ppm O_2 for 70 ingots prepared with Ca and $CaCl_2$, the metal prepared with Ca and Li as the co-reductants is markedly better. Actually, the difference might even be greater than this if another factor were considered. The first nine ingots in Table X (C-246 through 284) contain an average of 1235 ppm oxygen and the last ingots (C-288 through 308) contain an average of 1750 ppm O_2 . This is difficult to understand since all of the reductions were run with filtered lithium and massive calcium and magnesium metals, using identical procedures. However, the first nine ingots were prepared during April and May whereas the last five ingots were prepared during the month of June. Inasmuch as the Y-Mg alloy is noticeably more reactive in a humid atmosphere and the presence of small amounts of lithium makes it even worse, this may be a significant factor. This appears particularly so since the weather in Iowa prior to May 30th was unusually dry this year but has been extraordinarily damp and humid since that date, with more than an average amount of precipitation occurring over the latter period. These conclusions are corroborated by analysis of the trend in the oxygen content of those ingots prepared by the standard Ca and $CaCl_2$ reduction over the same period. Ingots prepared prior to June 1 contained an average of 400 ppm less oxygen than those produced since that date.

Other reductants: Because of the affinity of calcium and lithium for oxygen, several other variations in the reduction process have been tried but with little or no apparent success. One such experiment that was tried very early in the investigation was the reduction of YF_3 with magnesium exclusively. An excess of Mg was added to the charge for alloying purposes and CaCl_2 was added to flux the high melting MgF_2 that should have formed. Under the conditions of the experiment the results were entirely negative.

3.2.4 Refining of Y-Mg Alloy by Salt Extraction

A recent development that has resulted in a significant reduction in the oxygen content of yttrium metal is a refining process by which oxygen is extracted from the Y-Mg alloy. The slag is removed from a regular reduction and fresh YF_3 and CaCl_2 are added to the reaction vessel. After heating until both the alloy and salt phases are liquid, a tantalum or titanium stirrer is introduced to provide intimate contact between the two phases. Oxygen is extracted preferentially from the alloy into the salt phase, resulting in a decrease in oxygen content of the metal from 1500-3000 ppm down to 300-500 ppm O_2 in a single extraction. The details of these experiments and the physical chemistry of the extraction will be covered in a later report.

The basic principle on which the refining process operates is believed to be related to the chemical stability of YOF and its preferential solubility in YF_3 . The quantity of extractant required depends upon the amount of oxygen in the original alloy and the oxygen content of the YF_3 . The process has been shown to work equally satisfactorily on alloys obtained by a lithium reduction. In these experiments the extractant mixture consisted of YF_3 plus LiF. The reduction and the extraction can be accomplished in a single heating operation by adding a 50 to 75% excess of YF_3 to the charge.

While the oxygen content of the yttrium is considerably reduced by this technique, the corrosion of the titanium crucible is accelerated due to stirring and longer contact time. The titanium content of the yttrium thus prepared is 0.3 to 0.5 w/o. Experiments utilizing tantalum, molybdenum and vanadium crucibles indicate that the contamination by the reaction vessel can be eliminated or greatly reduced if desirable. Molten Y-Mg alloy dissolved less than 0.01 w/o Ta, 0.03 w/o Mo and 0.08 w/o V in two-hour contact periods.

The fluoride content of the alloy is not significantly affected by this extraction treatment. Metal prepared by reduction with calcium contains approximately 600 ppm fluoride before and after extraction while yttrium

prepared by lithium reduction contains about 1000 ppm fluoride.

Although the fluoride content is lowered significantly during vacuum arc melting, it is not removed completely. The use of YCl_3 as an extractant is currently being explored in an attempt to reduce both the oxygen and fluorine content of the metal. Based upon the results of a single experiment, the fluoride content of the metal can be reduced to 300 ppm and oxygen to 550 ppm by this method. Zone refining and electron beam melting are also being investigated as ways of removing fluoride.

An obvious disadvantage of the process described lies in the consumption of yttrium fluoride in the extraction step. Because of the economic value of this material, its recovery is of importance. If the ratio of CaCl_2 to YF_3 in the extractant is kept below a critical value, it has been found that all of the YF_3 can be recovered by leaching the CaCl_2 from the salt mixture with water and rehydrofluorinating the undissolved fluoride residue. The quality of the recovered YF_3 is equivalent to that of the starting material, with the exception of the presence of a few per cent of CaF_2 . This material was used satisfactorily as an extractant and also was reduced to the metal.

3.3 Purification of Yttrium by Distillation

From studies on inclusions in yttrium, it appears that oxygen is present in the metal in the form of yttrium oxyfluoride, and that at high temperatures in high vacua, yttrium oxyfluoride decomposes to yttrium fluoride and yttrium oxide. Vapor pressure studies on yttrium metal indicated that it would be possible to distill the metal at an appreciable rate at 2000°C. Under these conditions, the oxygen should remain behind as non-volatile residue. Such a procedure appeared to be doubly attractive in that it should also leave behind other impurities less volatile than yttrium (such as tantalum, titanium and zirconium) that are dissolved from the crucible in the reduction step. The first problem in this approach was to devise a furnace with sufficient insulation and pumping capacity to achieve a high vacuum at the anticipated distillation temperature of 2000°C. From a series of tests, a furnace was evolved in which 80 to 100 gram amounts of yttrium were successfully distilled. The distillation chamber is welded from 35 mil tantalum sheet, and is 1 5/8" in diameter and 9" long, with two collimator diaphragms 6 1/2" and 7" from the bottom. A 1/8" diameter hole in the lid allows evacuation of the distillation chamber, and yet is small enough to reduce back-diffusion of furnace gases when distillation

takes place. Two inches of the tube extends out of the insulated zone of the furnace and becomes the condenser; when the lower portion of the tube is at 2000°C during distillation, the condenser is at 1300 to 1400°C. The vacuum in the furnace is maintained below 2×10^{-5} mm at temperature, and has made possible oxygen contents in the condensates of from 120 to no higher than 350 ppm. Previous runs in which the pressure rose to 5×10^{-4} mm resulted in oxygen values of from 350 to 600 ppm. Carbon and nitrogen contents are 300 and 50 ppm, respectively, and the tantalum content was reduced from $> 1\%$ to < 300 ppm. Redistillation of the lower oxygen content metal under the same furnace conditions did not appear to improve the purity of the metal. Perhaps the most significant factor in preparing these samples of yttrium containing less than 150 ppm oxygen was the use of fine-grained graphite insulation (420 microns). High purity AGOT graphite turnings were outgassed at 2000°C to obtain a 2×10^{-5} mm vacuum at this temperature. Larger scale distillations are anticipated after the best conditions for this process have been determined.

References

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4. Analytical Chemistry of Yttrium Metal and Its Compounds

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R. Z. Bachman, W. A. Gordon, G. J. Kamin, and J. W. Goetzinger

Yttrium metal dissolves readily in the common mineral acids, except hydrofluoric, and exhibits only one oxidation state in aqueous solution. Consequently, its analytical chemistry is relatively uncomplicated and the determination of the usual impurities, with the exception of oxygen and fluorine, in yttrium metal and its compounds presented few problems. Standard analytical methods, with little or no modification, were used for the determination of carbon, nitrogen, iron, zirconium, titanium and nickel in yttrium. No effort was made to determine lanthanide impurities in yttrium since this could be done spectrographically.

Brief descriptions of the methods employed are given in the following sections. Copies of the procedures are available.

4.1 Determination of C, N, Fe, Zr, Ti, Ni, and F in Yttrium Metal

Carbon: Carbon was determined by two methods, both of which were equally satisfactory. Initially, a gravimetric method was used in which the metal sample was burned in a Fisher Induction Carbon Apparatus and the carbon dioxide was collected on Ascarite and weighed. Carbon

was also determined conductimetrically using a Leco Conductometric Carbon Analyzer, Model No. 515. The sample was burned in a Fisher Induction Furnace. In the latter case the induction furnace was modified so that the oxygen began to flow at the same time power was supplied to the coil rather than 20 seconds later. This was done so that the mercury would not be pulled back through the fritted disks in the Conductometric Carbon Analyzer.

Nitrogen: The nitrogen was determined by titration with 0.01 N hydrochloric acid following dissolution of the sample in hydrochloric acid and distillation of the ammonia from sodium hydroxide into a solution containing boric acid and methyl purple.

Iron: Iron was determined spectrophotometrically as the tris(1, 10-phenanthroline)iron(II) complex. The procedure used is described by Fortune and Mellon.¹

Zirconium: Zirconium was determined spectrophotometrically using sodium alizarin sulfonate as the reagent. The procedure used is described by King and Owens.²

Titanium: Titanium was determined spectrophotometrically using the titanium peroxide color in a solution containing sulfate. The procedure is described by Sandell.³

Nickel: Nickel was determined spectrophotometrically by forming the 4-methyl-1,2-cyclohexanedionedioxime complex at pH 4.5 in an acetate buffered solution, extracting it into chloroform, and reading the absorbance of the chloroform solution.⁴

Fluoride: The distillation of silicon tetrafluoride from a perchloric acid solution was found to yield consistent and apparently satisfactory results when followed by a spectrophotometric fluoride determination using the bleaching of the zirconium complex with sodium 2-(p-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6-disulfonate (SPADNS).⁵ Two types of distillation apparatus were used. In the first type used, air was swept through the apparatus during the distillation, and the liquid level and temperature were controlled by the dropwise addition of water. The second type of apparatus used was the type described by Huckabay, Welch and Metler,⁶ in which steam was swept through the apparatus. Temperature was held constant by surrounding the distillation flask with a jacket containing refluxing tetrachloroethane. The same results were obtained from both types of apparatus. However, the second type demanded less operator attention.

The pyrohydrolytic method did not prove too satisfactory for the determination of fluoride in yttrium because the metal sometimes failed to oxidize. Three sets of conditions have been used to convert

the metal to the oxide. They are:

1. Place the sample in a cold furnace and increase temperature to about 1000°C in one hour while passing moist air over the sample.
2. Place the sample in a cold furnace and increase temperature to about 1000°C in one hour while passing moist oxygen over the sample.
3. Place the sample in a hot furnace (about 1000°C) and pass moist oxygen over it.

The samples were oxidized most completely when using the first set of conditions, but the fluoride results were quite low even when the air was replaced by oxygen after the metal had oxidized.

Previous work showed that if the sample was placed in a cold furnace and the temperature increased at the rate of about 100°C per hour, with moist air passing over the sample, both the conversion to the oxide and the fluoride evolution were complete.

4.2 Determination of Oxygen in Yttrium Metal

Since the presence of oxygen in yttrium metal exerts a marked deleterious effect on the physical and mechanical properties of this metal, the quantitative determination of oxygen has been extensively

studied. As a result of these investigations, three independent techniques for performing this analysis have been devised. These are based on: (a) vacuum fusion; (b) inert-gas fusion; and (c) emission spectroscopy. The emission spectrometric method is discussed elsewhere (see section 5).

4.2.1 Vacuum Fusion

The vacuum fusion technique is based on the reaction, in a vacuum, of the oxygen in a metal with carbon to form CO. If this reaction is allowed to proceed in a mobile liquid bath in which an adequate amount of carbon is dissolved, quantitative evolution of the CO is achieved in about 30 minutes. The metal best suited for this bath is platinum. The platinum bath or flux is added to the reaction crucible simultaneously with the sample. Since hydrogen and nitrogen are also evolved under these conditions, the CO content of the gases evolved is determined by conventional low pressure oxidation to CO_2 and separation by selective freezing.⁷ From the pressure-volume product of the separated gas, the weight per cent of oxygen can be calculated.

Pertinent experimental details for performing these determinations are summarized below.

Equipment used: NRC Equipment Corporation 912S Vacuum Fusion
Gas Analysis Apparatus.^{7, 8}

Crucible: 7/8" diameter graphite crucible and funnel, United
Carbon Products Co., No. C-625, F-703, packed in -200
mesh graphite powder (UCP-2).

Furnace: Graphite parts assembled in quartz tube suspended
inside air cooled Pyrex shell.⁹

Power source: Lepel High Frequency Corporation Model T-2.5B
induction heating unit.

Bath material: Platinum (12 gauge wire) to total weight of ten
times weight of samples to be analyzed.

Flux: 500 mg platinum wire (12 gauge) added with each sample.

Sample weight: 100-500 mg, depending on expected oxygen content.

Outgassing:

Furnace: Temperature raised in one hour to 2400°C, then
maintained 2 to 3 hrs at 2400°C.

Platinum bath: 45 min to 1 hr at 1900°C or until pressure in
furnace has reached blank pressure level (1×10^{-6} mm Hg).

Sample: 15 min to 1 hr at 1850-1900°C, varying with oxygen
content of yttrium metal. Outgassing continued until the
final pressure in furnace returns to initial pressure.

Analysis of gas evolved: Conventional low pressure oxidation and selective freezing.^{7, 8} All values reported corrected for the oxygen content of the platinum flux as well as the usual furnace "blank".

Blank:

Furnace: 2-3 ppm oxygen/gram yttrium

Flux: 5-7 ppm oxygen/gram platinum

4.2.2 Inert Gas Fusion

The inert gas fusion technique has been applied to the determination of oxygen in yttrium metal and yttrium fluoride. The commercially available Leco apparatus is used and the procedures recommended by the manufacturers are followed with several modifications. A platinum bath is employed with an operating temperature of 2200°C. The system is preheated for two minutes, a sample of metal containing 100 to 200 γ of oxygen is introduced into the crucible, the heating is continued for two minutes, the power is shut off, and the system is swept for five minutes. The oxygen is measured conductimetrically as carbon dioxide. The blank is constant for a given crucible and bath, and ranges from 20 to 40 γ oxygen. Table XI shows a comparison of results obtained by this technique and those by the vacuum fusion and spectroscopic techniques.

Yttrium fluoride has also been analyzed by the above technique. The only difference is that for the analysis of the fluorides, a magnesium oxide trap is used to remove any silicon tetrafluoride that may be formed during the heating cycle. Table XIII shows a comparison of these results with those achieved by the vacuum distillation and KBrF_4 methods.

4.2.3 Emission Spectrometric

The emission spectrometric method for the determination of oxygen in yttrium metal is discussed in Section 5.3. Table XI shows a comparison of emission spectrometric results with those obtained by the other techniques.

4.2.4 Bromine Insoluble Residue

A determination of the residue left when yttrium metal was dissolved in a mixture of one part bromine and four parts methanol gave a semi-quantitative estimation of the amount of oxygen present in yttrium sponge. The method was also used on arc-melted yttrium metal.

Two of these residues were analyzed for yttrium, oxygen, and fluorine. In one case, the relative amounts of these elements corresponded to yttrium oxide and in the other case to yttrium oxyfluoride.

A third sample of residue analyzed for yttrium and fluoride also appeared to be largely yttrium oxide. Analysis of the residue also showed it to contain most but not all of the carbon, nitrogen, iron, titanium and zirconium originally present in the metal.

The samples were placed in a two-necked round-bottom flask fitted with an addition funnel and a water-jacketed reflux condenser. A small portion of the bromine and methanol mixture was added from the addition funnel and after the initial vigorous reaction had subsided, enough additional bromine and methanol mixture was added to dissolve the remainder of the metal. After the reaction stopped, the solution was filtered through a sintered glass filter crucible and the residue dried and weighed.

Extreme caution must be exercised when handling the bromine-methanol mixture.

4.2.5 Comparison of Analytical Results

Table XI shows a comparison of analytical results obtained on several samples of Ames yttrium metal. The results show acceptable agreement.

Table XI

Determination of Oxygen in Yttrium Metal

Sample	% Oxygen		
	Spectrographic	Vacuum fusion	Inert gas fusion
Y metal	—	0.140	0.145
	—	.189	.178
	—	.168	.175
	—	.103	.096
	0.074	—	.073
	.118	—	.113
	.166	—	.155
	.163	.162	.156
	.052	—	.040
	.048	.035	.033
Y Sponge	.042	.032	.033
	.034	.035	.031
		.040	.038
		.043	.043

— not analyzed

4.3 Determination of Total Oxygen Content of Yttrium Fluoride

Since the unreacted oxide or oxyfluoride content of yttrium fluoride appears to be one of the major sources of oxygen impurity in the yttrium metal, it is necessary to control the total oxygen content of the fluoride within tolerable limits. Four different techniques have been applied to this determination. These are based on: (a) vacuum distillation; (b) inert gas fusion; (c) reaction with KBrF_4 ; and (d) emission spectroscopy.

4.3.1 Vacuum Distillation Method

The vacuum distillation method is based on the observation that both yttrium oxide and yttrium oxyfluoride quantitatively liberate their oxygen content as carbon monoxide when these compounds are heated at 1800 °C in a graphite crucible in vacuo. Under certain experimental conditions the same reactions proceed quantitatively when these oxygen containing compounds are found as impurities in yttrium fluoride. Measurement of the quantity of carbon monoxide evolved therefore affords a means for determining the total oxygen content of the fluoride.

The vacuum distillation technique is basically a modification of the vacuum fusion method for the determination of oxygen in metals.

The primary difference is that the fluoride sample is actually distilled and recondensed in the carbon crucible in which the chemical reduction reactions take place.

The observation that quantitative liberation of the oxygen content of the Y_2O_3 and YOF impurity in the fluoride can be achieved suggests that both compounds remain in the hot part of the carbon crucible while the fluoride is volatilized. Although YOF has a relatively high vapor pressure, recent experimental evidence¹⁰ indicates that the compound disproportionates into the refractory Y_2O_3 and volatile YF_3 when it is heated in vacuo at temperatures between 1500-1800°C. Thus both oxygen containing compounds tend to be retained in the hot crucible, where contact with carbon causes evolution of the carbon monoxide.

Figure 12 shows a schematic diagram of the graphite crucibles used in these studies. An NRC Equipment Corporation Model 912S vacuum fusion apparatus forms the rest of the experimental facility. It is convenient to introduce YF_3 samples into the outgassed crucibles as compressed pellets. When 100 mg. pellets of YF_3 are introduced into the outgassed crucibles at 1800°C, the pellets melt and distill within a few seconds. Most of the volatilized fluoride condenses on the graphite funnel, which forms an integral part of the crucible. The

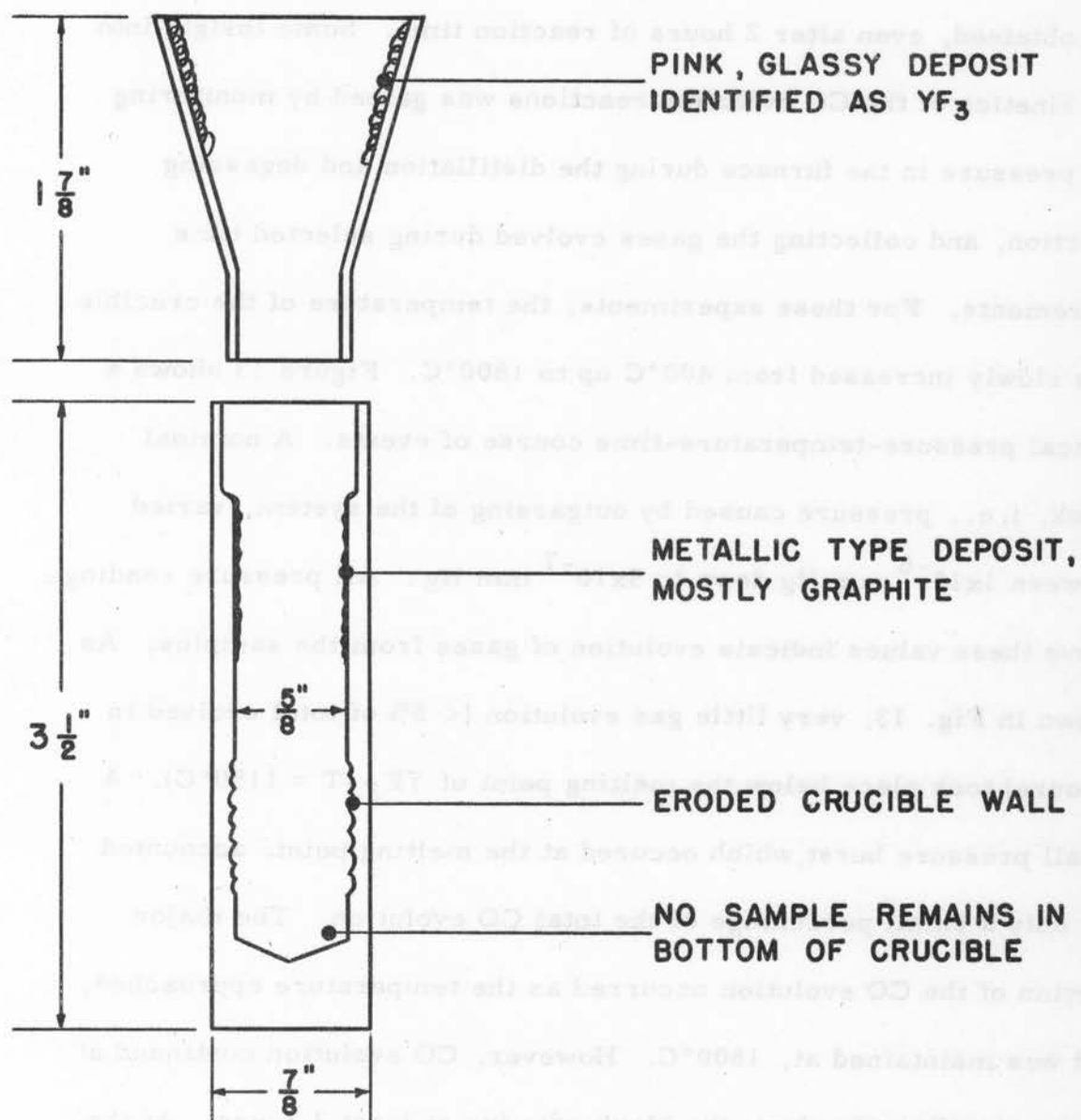


Fig. 12. Crucible Assembly.

temperature of the funnel is approximately 900 to 1000°C. Only traces of the fluoride are deposited on the glass walls of the furnace.

When pellets were introduced into the furnace at 1800°C, quantitative evolution of the total oxygen content of the fluoride sample was not obtained, even after 2 hours of reaction time. Some insight into the kinetics of the CO evolution reactions was gained by monitoring the pressure in the furnace during the distillation and degassing reaction, and collecting the gases evolved during selected time increments. For these experiments, the temperature of the crucible was slowly increased from 400°C up to 1800°C. Figure 13 shows a typical pressure-temperature-time course of events. A nominal blank, i. e., pressure caused by outgassing of the system, varied between 1×10^{-6} mm Hg down to 5×10^{-7} mm Hg. All pressure readings above these values indicate evolution of gases from the samples. As shown in Fig. 13, very little gas evolution ($< 5\%$ of total evolved in 2 hours) took place below the melting point of YF_3 ($T = 1150^\circ\text{C}$). A small pressure burst, which occurred at the melting point, accounted for only a small percentage of the total CO evolution. The major portion of the CO evolution occurred as the temperature approached, and was maintained at, 1800°C. However, CO evolution continued at a rate significantly above the blank rate for at least 2 hours. At the

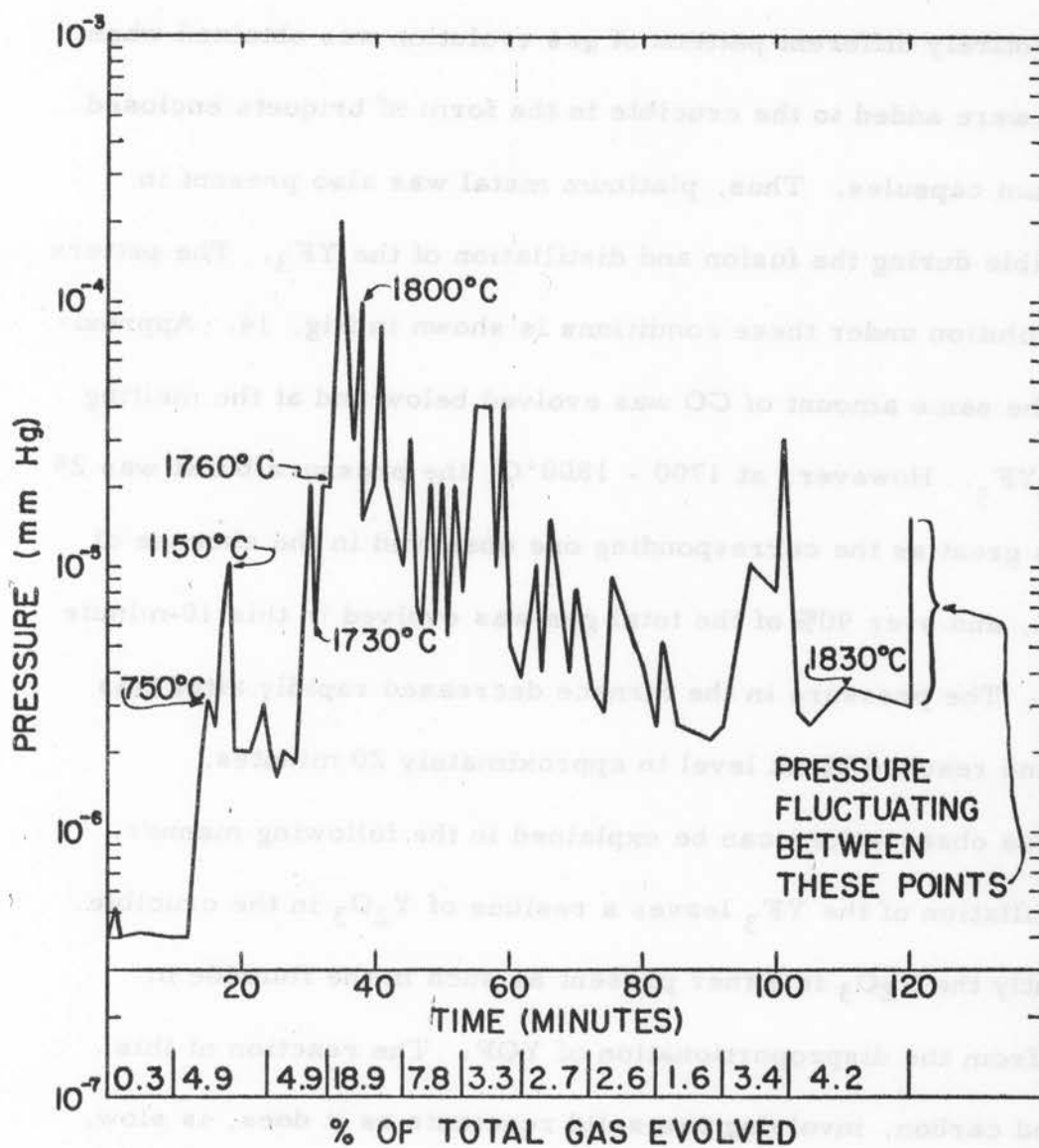


Fig. 13. Evolution of CO from YF_3 in Absence of Platinum.

end of this period, the total recovery of the oxygen of the sample, as evolved CO, was only about 50%.

An entirely different pattern of gas evolution was obtained when samples were added to the crucible in the form of briquets enclosed in platinum capsules. Thus, platinum metal was also present in the crucible during the fusion and distillation of the YF_3 . The pattern of CO evolution under these conditions is shown in Fig. 14. Approximately the same amount of CO was evolved below and at the melting point of YF_3 . However, at 1700 - 1800°C, the pressure burst was 25 times as great as the corresponding one observed in the absence of platinum, and over 90% of the total gas was evolved in this 10-minute interval. The pressure in the furnace decreased rapidly after this burst, and reached blank level in approximately 20 minutes.

These observations can be explained in the following manner. The distillation of the YF_3 leaves a residue of Y_2O_3 in the crucible. Apparently the Y_2O_3 is either present as such in the fluoride or results from the disproportionation of YOF . The reaction of this Y_2O_3 and carbon, involving two solid reactants as it does, is slow. Since the melting point of platinum is 1773.5°C, it appears that the presence of a liquid metal in the crucible provides a reaction medium and thus accelerates the reaction.

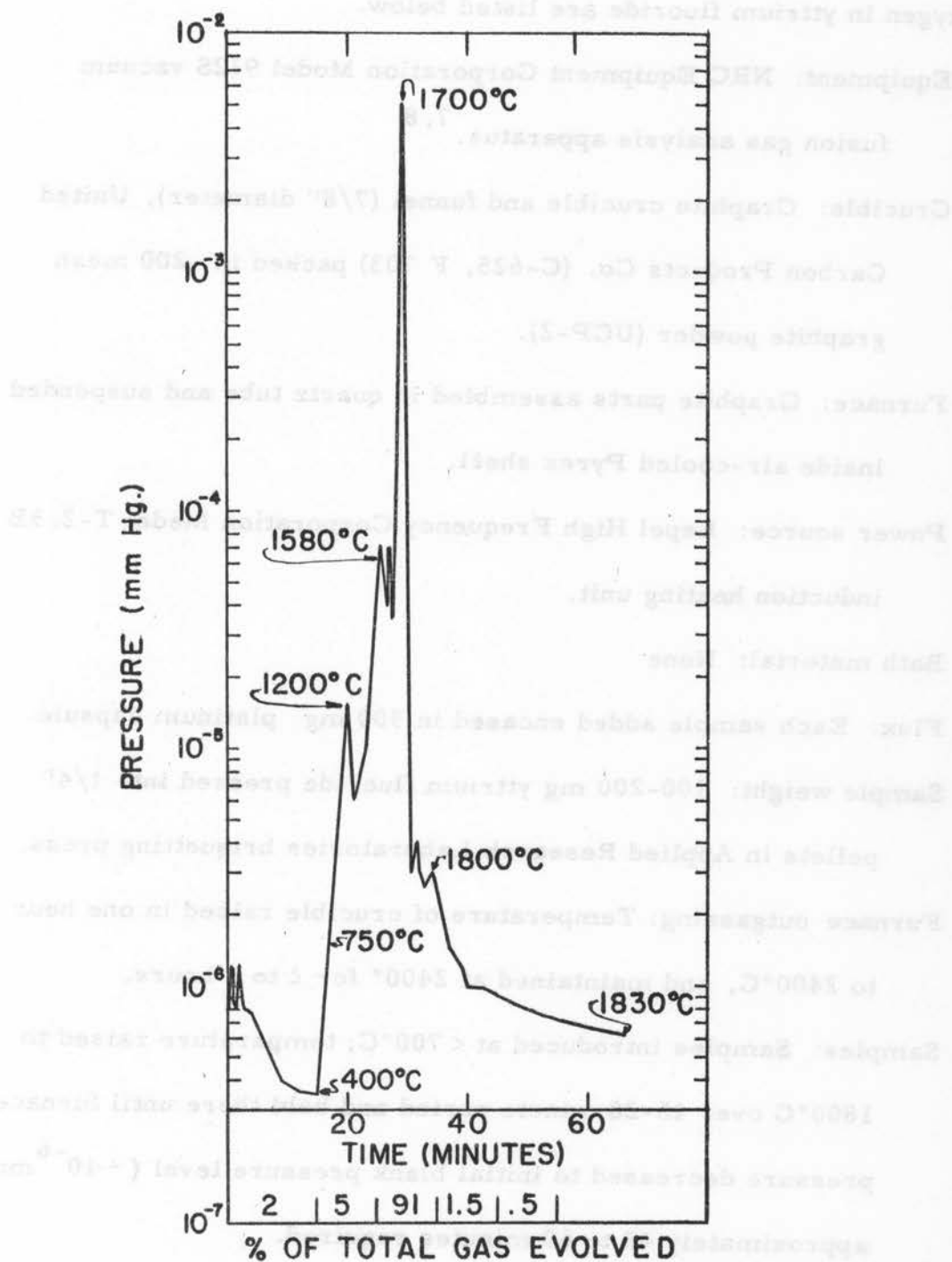


Fig. 14. Evolution of CO from YF_3 in Presence of Platinum.

Experimental conditions for vacuum distillation determinations of oxygen in yttrium fluoride are listed below.

Equipment: NRC Equipment Corporation Model 912S vacuum fusion gas analysis apparatus.^{7, 8}

Crucible: Graphite crucible and funnel (7/8" diameter), United Carbon Products Co. (C-625, F 703) packed in -200 mesh graphite powder (UCP-2).

Furnace: Graphite parts assembled in quartz tube and suspended inside air-cooled Pyrex shell.

Power source: Lepel High Frequency Corporation Model T-2.5B induction heating unit.

Bath material: None

Flux: Each sample added encased in 300 mg. platinum capsule.

Sample weight: 100-200 mg yttrium fluoride pressed into 1/4" pellets in Applied Research Laboratories briquetting press.

Furnace outgassing: Temperature of crucible raised in one hour to 2400°C, and maintained at 2400° for 2 to 3 hours.

Samples: Samples introduced at < 700°C; temperature raised to 1800°C over 15-20 minute period and held there until furnace pressure decreased to initial blank pressure level ($\sim 10^{-6}$ mm Hg); approximately 45 to 60 minutes required.

Analysis of gas evolved: Carbon monoxide only evolved from

YF_3 . Total PV product measured and corrected for gas content of platinum flux and furnace "blank".

Blank:

Furnace: 40-50 ppm/100 mg YF_3 .

Platinum capsule: 25 ppm/100 mg YF_3 .

Table XII summarizes the analytical results obtained on a series of synthetic samples prepared by blending a low oxygen content YF_3 with additions of pure Y_2O_3 or YOF . These blends were prepared by dry grinding in an inert atmosphere using a boron carbide mortar and pestle. The data in Table XII show that quantitative recoveries are obtained.

4.3.2 Inert gas fusion

See Section 4.2.2.

4.3.3 Emission Spectrometric

See Section 5.4.

4.3.4 High Temperature Fluorination

The high temperature fluorination technique proposed by Sheft, Martin, and Katz¹¹, in which fluorination is accomplished by means of molten KBrF_4 , has been applied to the determination of oxygen in

yttrium fluoride, yttrium chloride, and yttrium-magnesium alloys.

The reaction is carried out in an evacuated nickel chamber at 450°C.

The molecular oxygen evolved is measured manometrically after all

condensable gases are frozen out in liquid nitrogen cold traps.

Table XII

Summary of Vacuum Distillation Results in Yttrium-Fluoride-Oxygen Standards

Sample No.	Oxygen Content-ppm		No. of Determinations	% Recovery	Coefficient of variation
	Calc.	Exp.			
Y ₂ O ₃ additions					
1	2440	2460	13	101	4.7%
2	1310	1390	9	106	4.2%
3	870	1060	9	122	6.6%
YOF additions					
1	2890	2880	9	100	4.4%
2	1600	1730	9	108	3.2%
3	960	920	9	96	3.2%

The reaction chamber is constructed of nickel and has a nickel cap grooved for a Kel-F gasket. The cap is held in place by means of a stainless steel collar which can be water cooled to protect the Kel-F

gasket from damage during the heating cycle. Other types of gaskets, including "Teflon", aluminum, and copper, were not as satisfactory as Kel-F. Cooling the cap of the reaction chamber does not have any adverse effect on the reaction when KBrF_4 is used as the fluorinating reagent. The reaction chamber is attached to the vacuum line by means of 1/4" nickel tubing silver-soldered into the side of the reaction chamber and flared at the end. The flared end is joined to the vacuum line with a "Koncentric" union. A nickel diaphragm valve (Hoke 413) installed between the reaction chamber and "Koncentric" union permits the reaction chamber to be charged and evacuated, then closed and removed from the vacuum line, which makes it possible to use the same vacuum line with a number of reaction chambers. The vacuum line is similar to that described by Sheft, Martin and Katz.¹¹

The present operating procedure involves loading the clean, dry reaction chamber in a dry box with from 15 to 25 grams of KBrF_4 . The reaction chamber is then evacuated and prefluorinated at 450°C until the blank for a two-hour heating period falls to less than 20 γ of oxygen. The sample is then dropped into the reaction chamber while back flushing with helium. Finely divided samples are either loaded in the dry box or loaded quickly while the flow of helium is momentarily stopped. The latter procedure does not cause any significant increase in the blank

and is much simpler. The reaction chamber is then evacuated, heated for two hours and the evolved oxygen measured manometrically after freezing out all condensible gases in liquid nitrogen cold traps. The heating cycles are repeated until no more oxygen is evolved.

Experience with Ames Laboratory yttrium fluoride has indicated that oxygen is nearly quantitatively evolved in the first heating cycle. This was also found to be true for yttrium chloride and a number of the other metals and salts. Yttrium oxide reacts quantitatively in the first two-hour heating cycle, but yttrium metal reacts too slowly to be analyzed by this method.

It has been found that some yttrium fluoride samples do not react quantitatively even after twelve hours. This slow reaction rate has also been observed on samples of α -YOF and indicates that the form in which the oxygen is combined in yttrium fluoride samples may drastically affect the usefulness of the fluorination technique as an analytical method for oxygen in yttrium fluoride. This phenomenon is being investigated.

Yttrium nitride reacts with KBrF_4 to give molecular nitrogen and, on the basis of only a few yttrium nitride samples analyzed by both the fluorination and the Kjeldahl methods, the reaction appears to be quantitative. Other metals or salts might be expected to behave

similarly. Consequently, a simple manometric measurement of the gases evolved gives a nitrogen-oxygen total. In the case of yttrium fluoride, the nitrogen present was known to be very low and no correction was necessary. A modification of the present apparatus is planned which will permit the determination of both nitrogen and oxygen.

The results obtained on yttrium fluoride samples show a relative standard deviation of about 5%. The minimum amount of oxygen which can be detected is about 20 γ . The results obtained on yttrium fluoride samples have been generally lower than results on the same samples by vacuum distillation, spectrographic, and inert gas fusion techniques. The results obtained on several samples of Ames yttrium fluoride by the KBrF_4 and other methods are given in Table XIII.

4.3.5 Comparison of Analytical Results

Table XIII summarizes a comparison of analytical results obtained by the vacuum distillation, KBrF_4 , and inert gas fusion techniques. The values in parenthesis indicated duplicate values which showed large disagreements. In general, the vacuum distillation and inert gas fusion methods show good agreement. Since the emission spectrometric method is based on calibrations in which vacuum

distillation values are employed, the spectroscopic values are not included.

Table XIII
Determination of Oxygen in YF_3

Sample	%Oxygen		
	Vacuum Distillation	KBrF ₄	Inert Gas Fusion
A	—	.046	.045
B	—	.140	.149
C	.285	.200	.279
D	.186	.088	.163
E	.032	.017	.036
F	.030	.036	.048
G	.062	.050(.120)	.121
H	.433	.360	.431
I	.682	.640(1.0)	.694
J	.042	.049(.17)	.041

4.4 Determination of Fluorine in Yttrium Fluoride

Fluorine was determined in yttrium fluoride by pyrohydrolysis using U_3O_8 as an accelerator. The time of pyrohydrolysis was approximately thirty minutes. The weight ratio of accelerator to yttrium fluoride was one to one. The general procedure has been described by Warf, Cline, and Tevebaugh¹² and by Banks, Burke, and O'Laughlin.¹³

4.5 Analysis of Alloys

Binary yttrium alloys with titanium, magnesium, nickel, copper, and chromium were analyzed. The alloys were all dissolved in hydrochloric or nitric acid, except some titanium rich alloys which were dissolved in a hydrofluoric-nitric acid mixture.

Yttrium-titanium alloys: Both titanium and yttrium were determined in titanium-yttrium alloys. The titanium was determined spectrophotometrically as the peroxide complex. For large amounts of titanium, the spectrophotometer was balanced on a solution containing almost as much titanium as was present in the sample.¹⁴

It was necessary to separate the yttrium from the titanium in order to determine the yttrium. This was accomplished by forming the titanium peroxide complex and passing the solution through a column

of Dowex-50 resin. The yttrium remained on the resin and the titanium passed through. The yttrium was then removed with 3 N hydrochloric acid and determined by titration with the disodium salt of ethylenediaminetetraacetic acid or by precipitation as yttrium oxalate and ignition to the oxide.

Yttrium-magnesium alloys: Yttrium and magnesium were separated by forming the yttrium ethylenediaminetetraacetic acid complex at pH 4.5 and passing the solution through a column containing Dowex-50x8. The magnesium remained on the resin and the yttrium passed through. The magnesium was then removed from the resin with 3 N hydrochloric acid and titrated in the conventional manner with the disodium salt of ethylenediaminetetraacetic acid.

The yttrium was titrated in the presence of magnesium with the disodium salt of ethylenediaminetetraacetic acid at pH 4.5.

Yttrium-nickel alloys: In these alloys the nickel was separated and determined by precipitation with heptoxime according to the procedure of Voter and Banks.¹⁵ Following the separation, the excess heptoxime was destroyed and the yttrium titrated with the disodium salt of ethylenediaminetetraacetic acid.

Yttrium-copper alloys: These alloys were dissolved in nitric acid and determined electrolytically. The yttrium was then determined by titration with the disodium salt of ethylenediaminetetraacetic acid.

Yttrium-chromium alloys: The chromium in yttrium-chromium alloys was determined titrimetrically by a perchloric acid oxidation followed by the addition of excess standard iron(II) sulfate and the titration of the excess with standard cerium(IV) sulfate as described by Banks and O'Laughlin.¹⁶

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5. Analytical Spectroscopy of Yttrium

and Its Compounds

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The selection of high quality yttrium metal for reactor applications is based not only on a consideration of impurity constituents that influence the physical and mechanical properties of the metal, but also on the presence of impurities possessing high cross sections for thermal neutrons. This imposes the requirement that numerous impurity elements be determined, some with exceptionally high sensitivity. Since emission spectrometric methods of analysis are particularly useful for the simultaneous determination of a large group of elements at low concentration levels, this technique has been extensively used for the analysis of yttrium.

5.1 Determination of Rare Earth Impurities Commonly Associated with Purified Yttrium

A spectrographic method for the determination of the rare-earth impurities commonly associated with purified yttrium has been

described in a recent report.¹ Pertinent data for these determinations are summarized in Tables XIV and XV. The sensitivities achieved using this method are adequate for the routine analytical control of the ion exchange column separations. However, since the rare earths (Gd, Sm, Eu, Dy) which are most difficult to separate from yttrium possess some of the highest known cross sections for thermal neutrons, the judicious evaluation of the metal for reactor applications requires sensitivities in the 0.1 to 10 ppm range. Of these rare-earth impurities, gadolinium must be determined with the highest sensitivity; hence, efforts have been concentrated on extending the limit of detection for this element.

The most sensitive emission lines for gadolinium (3646.992\AA and 3422.466\AA) occur in the region in which cyanogen band radiation contributes a high background. Since this band radiation can be eliminated by excluding nitrogen from the arc column, the efficacy of exciting the samples in inert atmospheres was studied. The simple expedient of sweeping the analytical gap with CO_2 suppressed the band radiation sufficiently to allow the use of the more sensitive lines down to gadolinium concentrations of 10 ppm.

For more extensive studies involving the use of controlled atmosphere excitation, the chamber described by Hettel and Fassel²

Table XIV

Equipment and Operating Conditions for the Determination of Rare-Earth Impurities in Purified Y_2O_3

Spectrograph	Jarrell-Ash 3.4 meter Wadsworth grating spectrograph
Sample Charge	30 mg, 50% sample, 50% graphite
Electrode	Anode: 18 mm length of 6 mm diameter graphite rod with 2 mm deep cavity and wall thickness of 1/2 mm, supported on a 3 mm diameter graphite rod
	Cathode: 40 mm length of 3 mm graphite rod pointed on one end
Excitation	D.C. arc; 250 V, 18 amps, 4 mm analytical gap
Exposure Time	Complete sample consumption
Emulsions	Spectrum Analysis No. 1 (2900-4200), Kodak M (3800-4500)
Wave length	2950-4400 Å second order
Slit Width	40 microns
Emulsion Calibration	Two-step sector preliminary curve method
Densitometer	Applied Research Laboratories Comparator-Densitometer

Table XV

Data on Analytical Line Pairs

Line pair(A) °.*	Detection limit (%)	Useful conc. range (%)	Conc. index (%)	Background correction	Remarks
Sm 4334·149 Y 4291·034	0·05	0·10-2·0	0·8	No	Weak Dy line interferes with Sm at Dy ₂ O ₃ concentrations > 0·1%.
Gd 3350·482 Y 3377·711	0·005	0·04-2·0	0·23	No	A weak Dy line falls at the low wavelength side of Gd 3350 (≈0·05A). Unless sufficient resolution is available this line interferes at Dy ₂ O ₃ concentrations > 0·5%.
Gd 4327·104 Y 4291·034	0·05	0·10-2·0	1·4	No	
Tb 3218·93 Y 3182·42	0·02	0·04-2·0	0·79	No	
Tb 4318·85 Y 4315·46	0·05	0·10-2·0	1·5	No	Sm 4318·935 interferes at Sm ₂ O ₃ concentrations > 0·2%.

(continued)

Table XV (continued)

$\frac{\text{Dy } 3407 \cdot 80}{\text{Y } 3450 \cdot 95}$	0.005	0.05-2.0	0.5	No	There is a very weak Y line interference (equivalent to $\sim 0.005\%$ Dy_2O_3) with Dy 3407.80. A weak Y line at slightly lower wave-length ($\sim 0.25 \text{ \AA}$) may be used as an internal standard line for the visual estimation of Dy at low concentrations. When the intensity ratio is ~ 1 the Dy content is $\sim 0.01\%$. When the intensity ratio is 0.8 the Dy content is $< 0.005\%$.
$\frac{\text{Dy } 3407 \cdot 80}{\text{Y } 3469 \cdot 43^*}$	0.005	0.01-2.0	0.04	No	
$\frac{\text{Ho } 3453 \cdot 13}{\text{Y } 3450 \cdot 95}$	0.007	0.05-2.0	1.0	No	
$\frac{\text{Ho } 3453 \cdot 13}{\text{Y } 3469 \cdot 43^*}$	0.007	0.02-0.2	0.09	No	La 3453.168 interferes but La is very seldom present. Y 3453.45 does not interfere but may be mistaken for Ho 3453.13 unless care is taken.

(continued)

(continued)

Table XV (continued)

<u>Er 4007.967</u>	0.005	0.01-2.0	0.5	No
<u>Y 3955.095</u>	0.005	0.02-5.0	1.0	No
<u>Er 4007.967</u>	0.005	0.01-2.0	0.29	No
<u>Y 3987.497</u>	0.002	0.01-5.0	0.04	No

* Wavelengths marked with an asterisk were measured by the authors; all other

wavelengths were taken from the MIT wavelength tables.

was used. An auxiliary gas chamber was added to facilitate the mixing of the atmospheres employed. A study of the effect of pure gas atmospheres (O_2 , CO_2 , He and A) and various mixtures of these gases on the line to background ratios for Gd 3646.992\AA and Gd 3422.466\AA showed that mixtures of helium and oxygen offered the most promise. The maximum line to background ratios were observed when the atmosphere was blended from helium at 10 lbs pressure and oxygen at 2 to 4 lbs pressure. Under these conditions Gd 3646\AA exhibited slightly greater sensitivity, but Gd 3422\AA had a more constant line to background ratio. Using the experimental conditions given in Table XVI, a detection limit of 1 to 2 ppm was obtained for Gd 3422\AA . No improvement was noticed when a low voltage self-sustaining a.c. arc discharge was used for sample excitation.

A gain in detection sensitivity may also be obtained by concentrating the gadolinium with respect to the yttrium prior to spectrographic excitation. Since a detection limit of 1 to 2 ppm can be obtained by direct examination, only a concentration factor of approximately 20 is necessary to obtain the desired sensitivity. This degree of enrichment can be achieved by extraction techniques based on the nitric acid-tributylphosphate system.³

Preliminary experiments with this system indicated that the use of concentrated HNO_3 as the aqueous phase provided the best separation factor for gadolinium and yttrium. These experiments also showed that the gadolinium concentration in the aqueous phase increased upon extraction with tributylphosphate as long as the total rare earth concentration in the aqueous phase exceeded 5 g/100 ml. Below this value both gadolinium and yttrium apparently extracted to about the same extent.

Although separation factors of approximately 70 have been obtained using a continuous extractor, a simpler and more rapid method utilizing separatory funnels was found to give the necessary concentration factor of 20. In this procedure, 25 g of Y_2O_3 were dissolved in 100 ml of concentrated HNO_3 and extracted in a separatory funnel three times with equal volumes of tributylphosphate that had previously been equilibrated with concentrated HNO_3 . Care was taken to allow the system to return to equilibrium after each extraction. After the third extraction the rare earths remaining in the HNO_3 layer were precipitated with $\text{NH}_3 \cdot \text{H}_2\text{O}$, filtered and ignited to the oxide. Three replicate experiments using this technique provided an increase in the $\text{Gd}_2\text{O}_3/\text{Y}_2\text{O}_3$ ratio of $19.2\% \pm 0.4\%$. Additional extractions with TBP did not produce a greater concentration factor since the rare earth concentration in the

Table XVI

Excitation Conditions for the Determination of Gadolinium in Yttrium

Spectrograph	Jarrell Ash 3.4 meter Wadsworth Grating Spectrograph 15,000 rulings/inch
Electrodes	Anode: 1/4" diameter graphite rod with 3/16" dia. x 1/2" deep cavity. Undercut to 1/8" dia. 1/8" below cavity bottom. Cathode: 3" length of 1/8" graphite rod
Sample Charge	A blend of 120 mg of Y_2O_3 + 60 mg of graphite packed into the electrode cavity
Excitation	D.C. arc; 250 V, 30 amps, 4 mm analytical gap
Exposure Time	Complete sample consumption (~4 min.)
Atmosphere	3 lbs O_2 pressure + 10 lbs He pressure, premixed and swept through excitation chamber (continued)

Table XVI (continued)

Emulsion	Kodak type III-O plates
Wave Length	3000-4200 Å second order
Slit Width	30 microns
Emulsion Calibration	Two step sector preliminary curve method
Densitometer	Jarrell Ash Model 2100 comparator-microphotometer

HNO_3 fell below 5 g/100 ml after three extractions. The use of a higher Y_2O_3 concentration in the original HNO_3 solution increased the number of extractions which could be run before the total rare earth concentration fell below 5 g/100 ml. Although this increased the concentration factor, the reproducibility was much poorer ($\sim \pm 25\%$ of the amount present) and considerably more time was consumed by the extractions since the more concentrated solutions equilibrated slowly.

5.2 Determination of Common Impurities in Yttrium Metal and Sponge

Although the excitation of metal self-electrodes is usually the most expeditious technique for the spectrographic analysis of metals and alloys, the lack of reliable metal standards necessitates the conversion of the metal into a form for which accurate standards can be synthesized by chemical methods. Normally the simplest conversion procedure is the ignition of metal turnings or millings in air to form the oxide. In the case of yttrium, however, the ignition is attended with several experimental difficulties. Rather high ignition temperatures ($\sim 900^\circ\text{C}$) are required in order to obtain a reasonable rate of conversion. Not only are these high temperatures conducive to the loss of some of the more volatile impurities, but also

rather violent metal fires have occasionally occurred. Such fires can be prevented if the turnings are placed in a cold muffle and the temperature is slowly raised to approximately 950°C. In contrast, the dissolution of the sample easily provides a reproducible sample form for excitation. Likewise, solution standards are readily prepared by normal volumetric methods.

Although there are limitations to the direct excitation of solutions by the rotating disk⁴ or porous cup⁵ techniques, it is possible to achieve adequate sensitivity and excellent precision through the judicious selection of excitation parameters. The rotating disk electrode was selected for use in these studies because this technique imposes fewer restrictions on the power dissipation in the analytical gap. Moreover, the tendency for the solution to boil when high power discharges were used could be reduced by employing relatively large solution volumes in metal reservoirs.

The metal samples were dissolved in hydrochloric acid prepared from deionized water and anhydrous HCl. The solution was then diluted to give a sample concentration of 5 g/100 ml and an HCl concentration of approximately 2%. In some instances a black residue remained which dissolved upon the addition of 1 or 2 drops of concentrated nitric acid.

The base material for the standards was doubly, vacuum-arc-melted yttrium which was dissolved in the same manner as the samples. The impurities were added volumetrically from standard solutions to solutions of the base material. The standard solutions were made from reagent grade metals and salts that were available in a form suitable for weighing. All standard solutions were stored in polyethylene bottles to minimize contamination during storage.

The experimental conditions employed in exciting the solutions are summarized in Table XVII. For the determination of calcium and magnesium in yttrium sponge, the photographic plates were arranged so that a first order exposure was obtained over the region from 3600 to 4800 Å and a second order exposure over the region from 2400 to 3000 Å. A second order exposure was required to resolve the magnesium line from adjacent yttrium lines. These conditions allow the recording of satisfactory analysis lines for both calcium and magnesium with only one exposure. For the determination of boron it was necessary to use a Littrow prism spectrograph since sufficient intensity was not available at this wave length using the grating instrument.

Table XVII

Experimental Conditions for the Determination of Common Impurities in Yttrium Metal and Sponge

Spectrographs

Determination of Ca, Mg, Zr, Cu, Si and Ni

Jarrell-Ash 3.4 meter grating spectrograph-grating:

15, 000 rulings/inch.

Slit width: 45 microns

Determination of B:

Bausch and Lomb large Littrow spectrograph with quartz optics.

Slit width: 20 microns

Electrode Assembly

Rotating disk electrode assembly

Speed of rotation: 10 rpm

Disk electrode: National Carbon type L-4075

Counter electrode: 3/4" length of 1/8" graphite rod.

Analytical gap: 4 mm

(continued)

Table XVII (continued)

Excitation Source

National Spectrographic Laboratories "Spec Power"

Model 110-2S

Determination of Zr, Cu, Mg, Si, B and Ca:

Added resistance: 0 ohms

Added capacitance: 0.0025 μ fAdded inductance: 200 μ h

Spark power setting: 8

Primary voltage Variac setting: Adjust to obtain 6

breakdowns/half-cycle; approximately 54 to 56.

Auxiliary gap: 5 mm

Determination of Ni:

Added resistance: 3 ohms

Added capacitance: 0.0025 μ fAdded inductance: 300 μ h

Spark power setting: 8

(continued)

Table XVII (continued)

Primary voltage Vairac setting: adjust to obtain 4 breakdowns/half-cycle; approximately 48-50.

3 minutes

Exposure Time

Wave Length Regions and

Photographic Emulsions

Determination of Zr, Cu, Mg and Si:

Kodak III-0 plate, 2700-3300 Å 2nd order.

Determination of Ca and Ni:

Kodak M plate, 3400-4600 Å 1st order

Determination of Ca and Mg in sponge yttrium:

Kodak M plate, 3600-4800 Å 1st order: Kodak III-0

plate 2400-3000 Å 2nd order. (These may be exposed

simultaneously by placing the M plate on the low

wave length side of the plateholder and the III-0

plate on the high side.)

(continued)

Table XVII (continued)

Determination of B

Kodak III-0 plate, 2240-2788 Å.

Emulsion Calibration

Two step sector preliminary curve method using an

Fe spectrum exposed with a d.c. arc.

Densitometer

Jarrell-Ash Model 2100 microphotometer.

Table XVIII lists the pertinent data for the analytical line pairs used in these analyses. No extensive precision studies have been made; hence, values for precision are not given. However, replicate runs of a check standard over a considerable period of time indicate that the coefficient of variation should be less than $\pm 5\%$.

Some preliminary work using a spark ignited unidirectional pulsating arc ("Uniarc") for excitation has indicated that this type of excitation increases the sensitivity for silicon, magnesium and copper. Increased sensitivity may also result for some of the other impurities, but since these studies are incomplete, no definite recommendation can be made.

5.3 Determination of Oxygen in Yttrium Metal

Since the presence of oxygen in yttrium metal exerts a marked effect on the physical and mechanical properties of this metal, an analytical method is required that is capable of determining the oxygen content with accuracy and sufficient rapidity for normal production control. These requirements are fulfilled by the spectrographic method for oxygen in metals developed in this Laboratory; consequently, the basic technique has been adapted to yttrium metal. In this technique, a d.c. carbon arc discharge is used to extract

Table XVIII

Analytical Data for the Determination of Common Impurities in Yttrium Metal and Sponge

Line. Pair	Useful Conc. Range (ppm)	Estimated Det. Limit (ppm)	Conc. Index (ppm)	Remarks
Ca 3933.67 Y 3946.27	10-200	5	55	Fe 3933.605 Å interferes at Fe conc. > 0.3%
Ca 3933.67 Y 3930.66	100-1000	5	610	
Ni 3524.54 Y 3521.53	200-1500	100	1000	Zr 3524.538 Å does not inter- fere at Zr conc. < 1.0%
Mg 2852.13 Y 2850.65	30-1000	10	80	Fe 2852.13 Å is a weak line and does not interfere at Fe conc. < 0.2%
Zr 3020.47 Y 3018.95	1000-20,000	300	6600	Fe 3020.489 Å interferes at Fe conc. > 0.1%, however, Fe conc. is seldom this high
Zr 3019.84 Y 3018.95	2500-20,000	1000	4000	

(continued)

the oxygen content of the sample into a static argon atmosphere. A special electrode assembly is employed which provides a molten platinum-yttrium alloy after the arc is initiated. The oxygen content of the yttrium is rapidly evolved from this alloy as carbon monoxide. In d.c. carbon arc discharges in argon, the carbon monoxide is dissociated and the emission spectrum of oxygen is excited. The intensity ratio of $O_{7772\text{\AA}}/Ar_{7891\text{\AA}}$ is related to the oxygen content of the samples. All experimental details and "modus operandi" are exactly as those previously described⁶ for the determination of oxygen in titanium.

Two sets of standard samples were prepared in order to accurately establish analytical curves for this analysis. The starting materials for both sets of standards were vacuum arc melted buttons of yttrium metal weighing about 50 g each. In one set of standards a single button was drilled with 1/8" diameter holes into which a weighed amount of pure Y_2O_3 was packed. Metal plugs were then packed into each cavity and secured by a preliminary arc treatment. The button was then thoroughly arc melted in an atmosphere of purified helium with intervening "flipping" of the button to assure homogeneous distribution of the oxygen content. Successive dilutions of this standard were then made using the original base

material as a diluent and arc melting techniques to assure sample homogeneity. The second series of standards was prepared by adding pure Y_2O_3 in varying amounts to individual portions of a large arc melted button. Each portion was then arc melted as described above. The residual oxygen content in each series of standards was evaluated using the usual graphical procedures.⁷ The residually corrected analytical curve obtained by combining the data from the two series of standards is shown in Fig. 15. The fact that the data formed one continuous curve attests to the reliability of the residual correction. Further verification of the accuracy of the spectrographic results is found in the comparison of vacuum fusion and spectrographic analytical results as shown in Table XIX.

It should be mentioned that metal specimens have been encountered for which the oxygen analysis was questionable because of the low value. In all instances, when an effect of this nature was observed it was found that the calcium content of the metal was of the order of 0.2-1.0 weight per cent. It is not known whether the low values were a result of "gettering" by the vaporized calcium or of incomplete evolution of the oxygen content. This difficulty could be circumvented by "capping" the sample with an additional 0.25 gms of platinum metal formed into a disc.

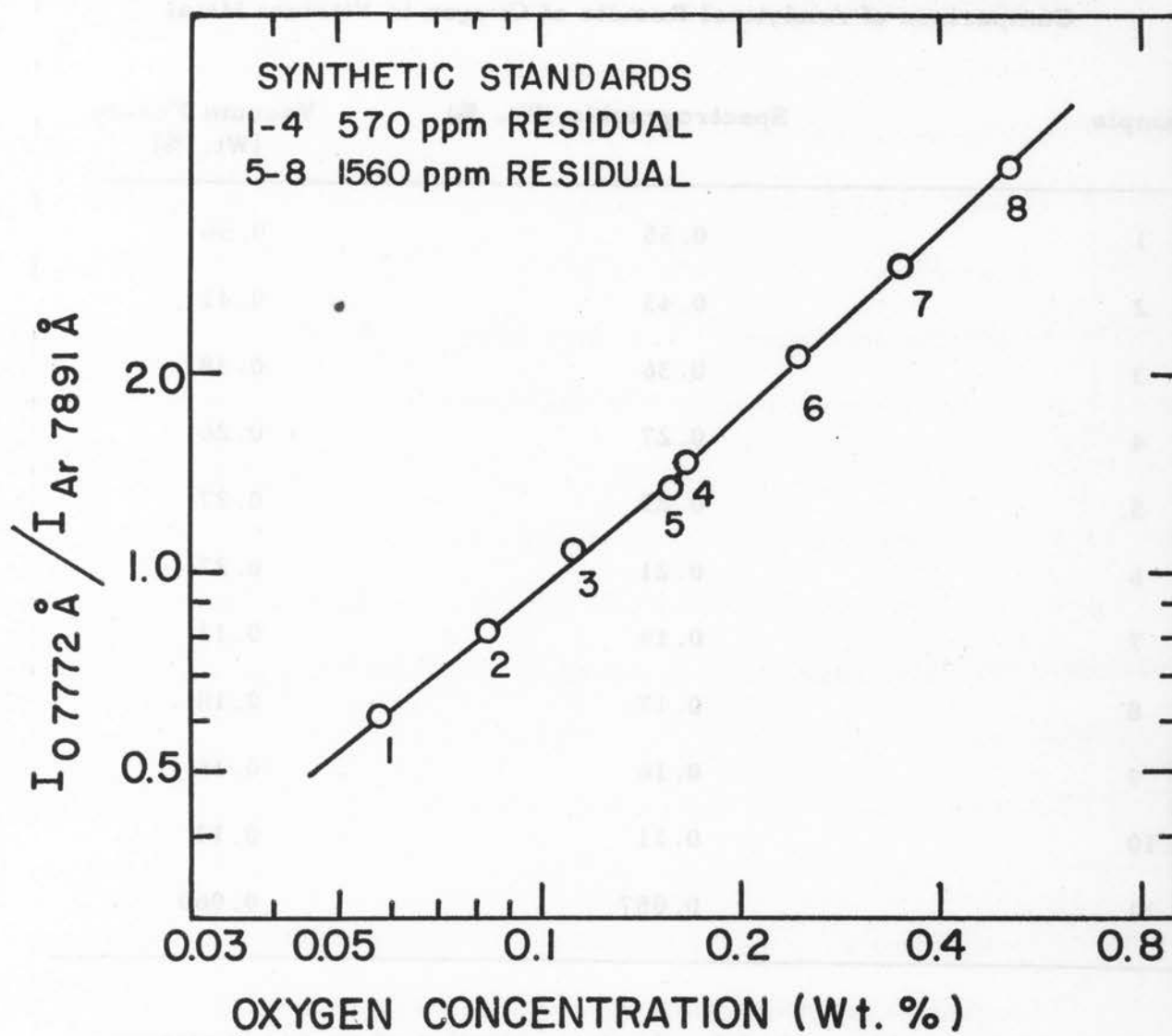


Fig. 15. Analytical Curve for the Determination of Oxygen in Yttrium Metal.

Table XIX

Comparison of Analytical Results of Oxygen in Yttrium Metal

Sample	Spectrographic (Wt. %)	Vacuum Fusion (Wt. %)
1	0.55	0.56
2	0.43	0.41
3	0.36	0.38
4	0.27	0.26
5	0.25	0.27
6	0.21	0.27
7	0.19	0.13
8	0.17	0.18
9	0.16	0.16
10	0.11	0.13
11	0.057	0.060

The spectrographic method for the determination of oxygen in yttrium has been used extensively in this Laboratory for routine analyses with a coefficient of variation of about $\pm 5\%$. Duplicate samples have generally

agreed to within ± 10 relative per cent. The effects of oxide segregation on the analytical results have not been evaluated.

5.4 Determination of the Total Oxygen Content of Yttrium Fluoride

The spectroscopic method is a modification of the procedure employed for the determination of oxygen in yttrium metal (Sec. 5.3). The yttrium fluoride samples are formed into briquets and placed in undercut, receptacle-type graphite electrodes that form the anode of a d.c. arc discharge in a static atmosphere of pure argon. The high temperatures generated by a 30 ampere arc discharge are effective in liberating most of the oxygen from the sample specimen. The oxygen triplet at 7772\AA is simultaneously excited by the arc discharge and the spectra are recorded photographically.

In the interest of measuring the total oxygen content of the samples, it would be desirable to volatilize the sample completely during the excitation phase. Unfortunately, excessive volatilization of the fluoride matrix not only produces intense YF band spectra which enhances the background, but also suppresses the excitation of the oxygen triplet and the argon internal standard line. It is therefore necessary to employ arcing conditions and an electrode design that will cause maximum evolution of the oxygen content and minimum fluoride volatilization.

During the earlier phases of the yttrium program at the Ames Laboratory, the lack of reliable standards for calibration purposes made it necessary to employ empirical $O_{7771\text{\AA}}/Ar_{7891\text{\AA}}$ intensity ratios as a semiquantitative measure of total oxygen content. For these measurements 100 mg briquets were arced in the usual manner. Under these conditions, the "blank", consisting of background and oxygen contamination from the system, contributed from 1/3 to 1/2 of the total intensity ratio. Since the blank could not be accurately reproduced, the intensity ratio values lost their significance at the lower oxygen concentrations. Figure 16 shows that at best the measurements had only semiquantitative significance between intensity ratios of 0.5 and 1.5. A solution to the problem of inadequate signal/blank ratio became apparent when it was observed that a 5-fold increase in this ratio could be obtained by performing the excitations at reduced pressure rather than under an atmospheric pressure of argon. This enhancement in the signal to blank ratio appears to be the result of increased efficiency in exciting the oxygen triplet emission and in extracting the oxygen content from the sample.

In order to obtain acceptable precision, further refinements in the sample handling procedure had to be introduced. In the technique as employed for metal samples, a series of 12 samples are excited

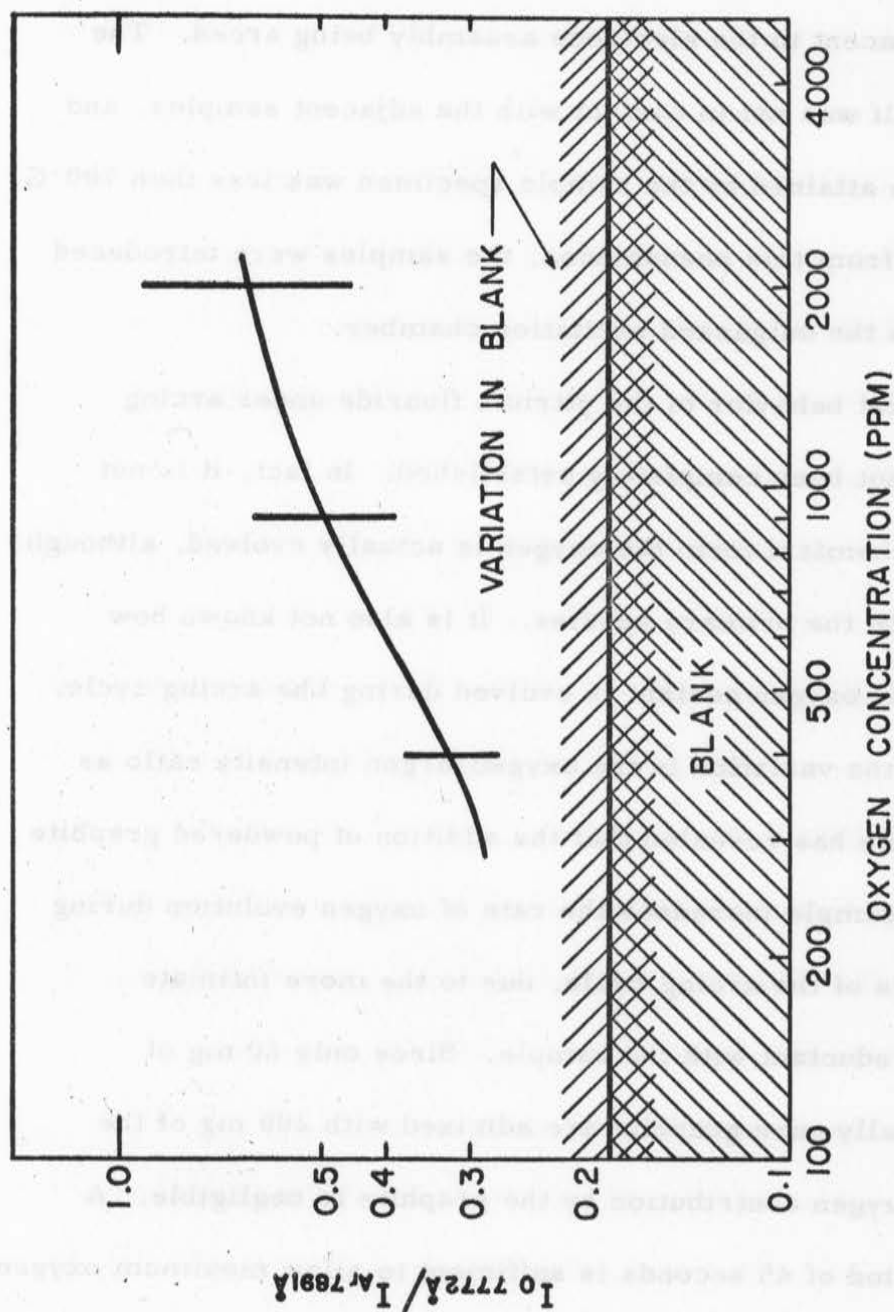


Fig. 16. Relation Between Empirical Intensity Ratios and Approximate Total Oxygen Concentration in Yttrium Fluoride.

sequentially in the chamber. In the case of yttrium fluoride samples, it was observed that some of the oxygen content was liberated from the samples adjacent to the electrode assembly being arced. The arc plasma itself was not in contact with the adjacent samples, and the temperature attained by the sample specimen was less than 700°C . To avoid error from this phenomenon, the samples were introduced individually into the outgassed excitation chamber.

The chemical behavior of the yttrium fluoride under arcing conditions has not been completely established. In fact, it is not known in what chemical form the oxygen is actually evolved, although CO appears to be the primary species. It is also not known how much of the total oxygen content is evolved during the arcing cycle. Observation of the variation in the oxygen/argon intensity ratio as a function of time has revealed that the addition of powdered graphite to the fluoride sample increases the rate of oxygen evolution during the early phases of the arcing cycle, due to the more intimate contact of the reductant with the sample. Since only 20 mg of spectrographically pure graphite are admixed with 200 mg of the fluoride, the oxygen contribution by the graphite is negligible. A pre-arcing period of 45 seconds is sufficient to allow maximum oxygen evolution from all samples studied.

Since the chemical state of occurrence of the oxygen content of fluoride samples probably governs the degree of evolution of the oxygen content during the arcing process, the preparation of reliable synthetic standards presupposes a knowledge of how the oxygen is distributed in a sample. In the absence of definite knowledge on the state of occurrence, it may be assumed that the oxygen occurs either as Y_2O_3 or YOF or mixtures of these compounds. If standards prepared from either form of contaminant produce equivalent intensity ratios, then the establishment of valid calibrations would be simplified. To test the feasibility of this approach, two series of standards were prepared, using Y_2O_3 as the oxygen contaminant in one series, and YOF as a contaminant in the second series. These standards were prepared by mechanically blending the contaminants with a highly purified YF_3 base. This blending was performed by dry grinding under an inert atmosphere. A boron carbide mortar and pestle was employed. Analytical data obtained from these standards have not provided consistent results, either among themselves, or in comparison with values obtained by independent chemical methods (see Sections 4.2.2 and 4.3). Accordingly, considerable caution must be exercised in the quantitative interpretation of results based on synthetic standards. It is not

unreasonable to expect that small differences in the chemical, crystalline, or physical constitution of the samples may exert a significant influence on the fraction of the total oxygen which is evolved during the arcing cycle. Intensity ratio data obtained from samples of similar preparative history, i.e., Ames Laboratory yttrium fluoride, are reproducible and are consistently related to the total oxygen content of the sample. Figure 17 shows an analytical curve prepared by plotting the observed $O_{7775\text{\AA}}/Ar_{7891\text{\AA}}$ intensity ratio as a function of total oxygen concentration as determined by the vacuum distillation technique (see Section 4.3.1). The length of the crossed lines in the plot signify the uncertainties in the observed intensity ratios and the oxygen concentrations as determined by vacuum distillations.

Except for a few minor modifications, the apparatus, electrode assembly; and mode of operation used in this procedure are the same as those described previously.^{1,2} A demountable port assembly, 2 cm in diameter, was constructed in the chamber top directly over the arcing position (Fig. 18). This port assembly serves a twofold purpose. After completion of the electrode outgassing operation, the port assembly is removed while the chamber is flushed with argon. This reduces the back diffusion of air into the chamber,

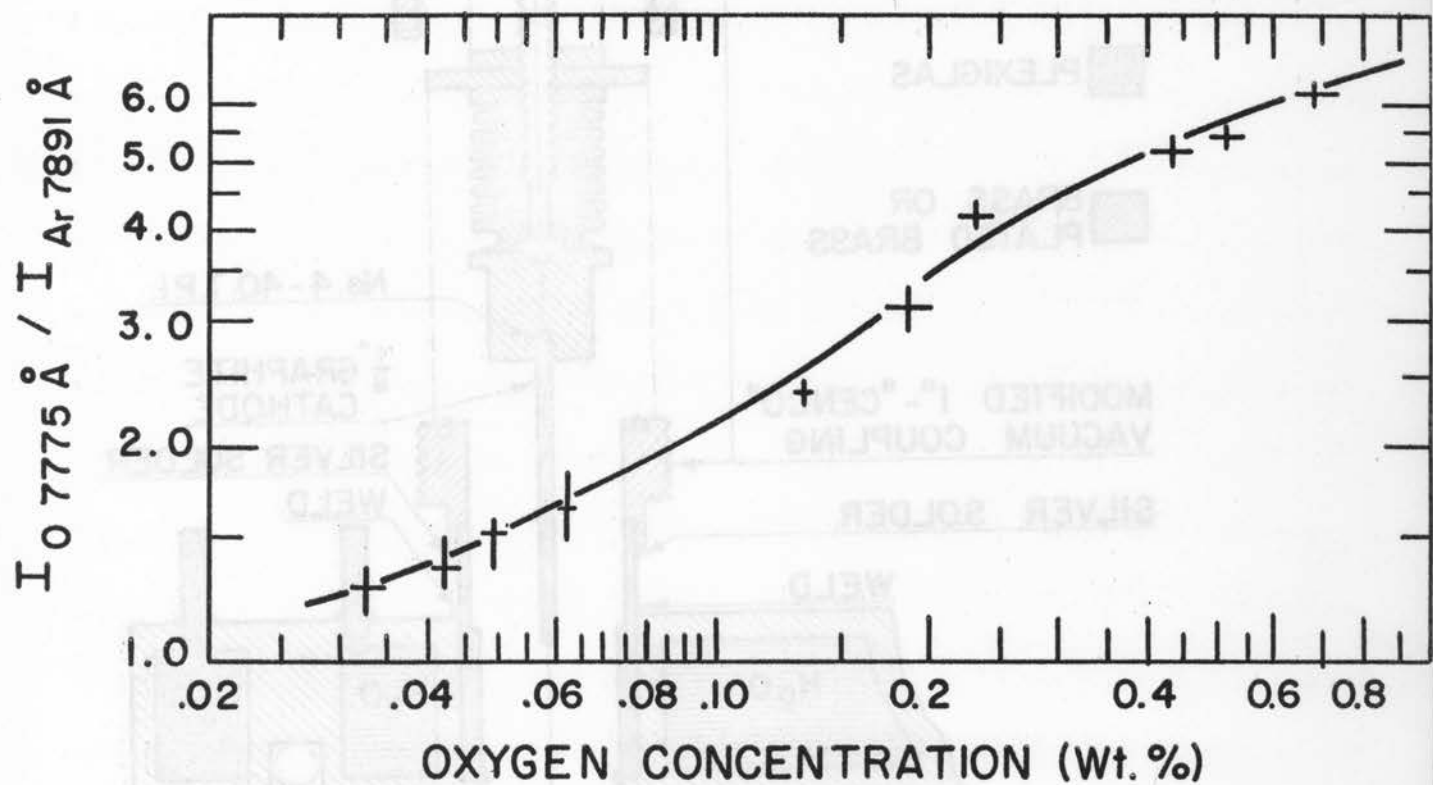


Fig. 17. Analytical Curve for the Determination of Oxygen in Yttrium Fluoride.

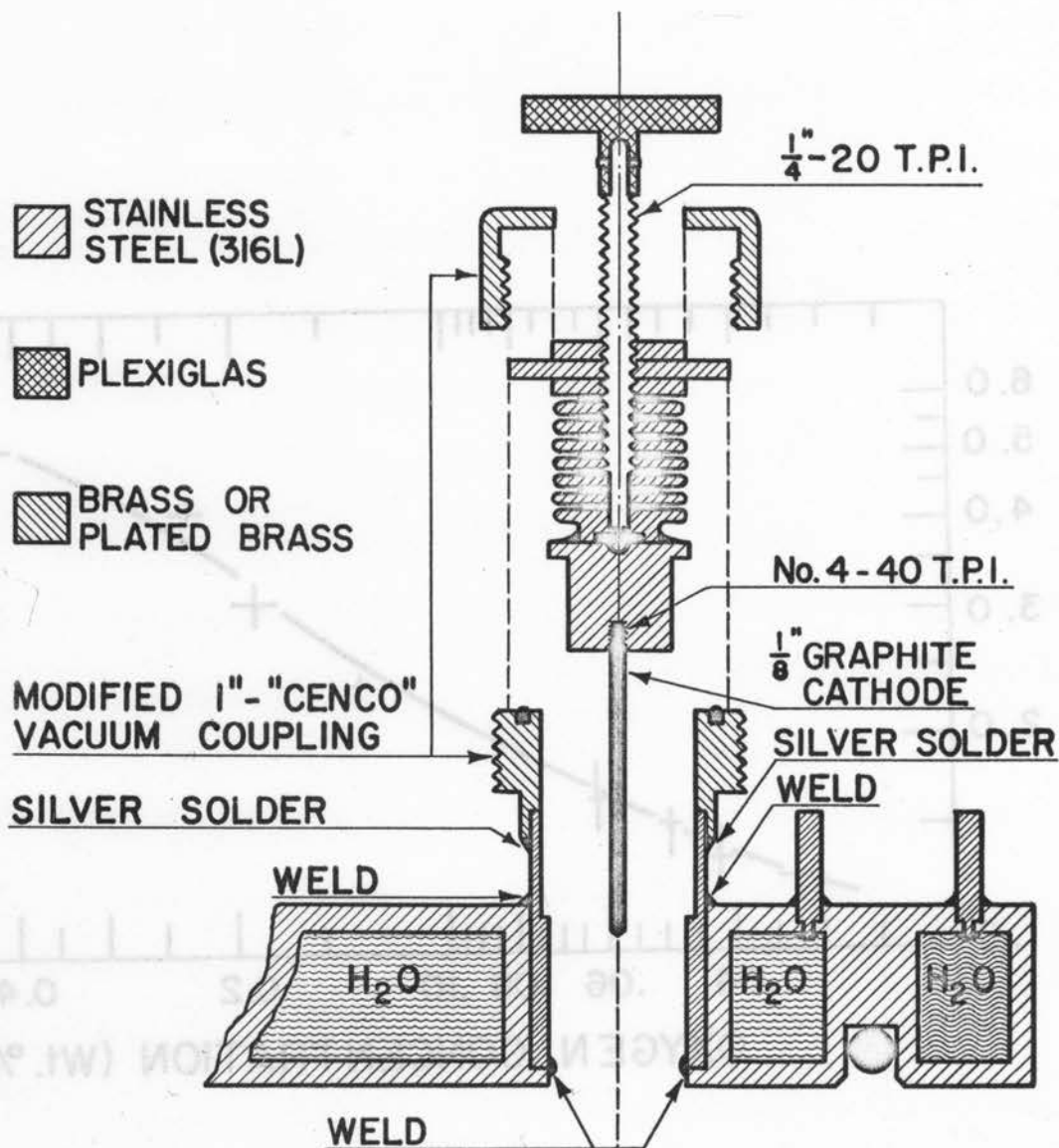


Fig. 18. Demountable Port Assembly for Excitation Chamber.

The sample is then transferred to the electrode receptacle through a length of glass tubing which fits over the sample electrode. After the port assembly is remounted, the chamber is evacuated. Pure argon is then admitted until a pressure of 125 mm is reached.

The samples are introduced into the electrode receptacle as 1/4 inch diameter briquets weighing 200 mg. These briquets are formed in an Applied Research Laboratories briquetting press from a blend of 10 parts sample to 1 part powdered graphite.

The electrode receptacle has also been slightly modified. The floor of the receptacle portion has a 35° taper. During the arcing cycle the molten fluoride forms a globule which tends to localize itself in this depression. The electrode assembly is arced at 30 amperes with an argon supporting atmosphere at 125 mm pressure. Maximum oxygen evolution occurs during the 45 second prearc period. The arc is then terminated, and an auxiliary graphite electrode is rotated into position for the actual spectrographic exposure. In this manner the complex band spectra, characteristic of yttrium fluoride, are avoided. Duplicate exposures of each sample are made to increase the precision of measurements. The average of duplicate observations have shown a coefficient of variation of $\pm 5\%$ of the amount present.

5.5 Determination of Yttrium in Ores, Concentrates, and Column Fractions

The selection and subsequent concentration of ores used as yttrium source materials requires a suitable analytical method for determining major amounts of yttrium. The great similarity in the chemical properties of yttrium and the rare earth group of elements prohibits the use of classical chemical methods of analysis. However, two independent spectrometric methods have been developed which are suitable for this analysis. A method involving the use of x-ray fluorescent techniques has been recently reported by Heidel and Fassel.⁸ An emission spectrometric method based on d.c. carbon arc excitation has also been reported by Fassel.⁹ Although the latter procedure provided acceptable precision and accuracy, the method has been superseded by a technique based on the use of a rotating disk electrode for the excitation of the samples in solution form. In this manner the preparation of a homogeneous mixture of the sample and the added internal standard element is simplified. Likewise, the use of controlled a.c. spark excitation contributes to improved precision.

Since yttrium greatly resembles the lanthanide elements in both its physical and chemical behavior, it is appropriate that a member of this series be chosen as an internal standard. Likewise,

it is desirable to use an element which has numerous spectral lines which are free of interference from other elements normally encountered in yttrium ores. Since cerium not only fulfills these requirements and also resembles yttrium in its excitation behavior, it was chosen as the added internal standard element. A 9-fold addition of the cerium to the sample was used in order to render negligible the effect of any cerium originally present in the sample and to increase the effectiveness of the cerium as a spectroscopic buffer.

For the rotating disk method, 50 mg of the sample are dissolved in 2 ml of nitric acid followed by the addition of 450 mg of cerium as cerous nitrate solution. The latter is prepared by dissolving ammonium hexanitrate cerate in 5% HNO_3 and reducing the cerium by adding 30% H_2O_2 until the red-orange color disappears.

The pertinent experimental conditions for this determination are summarized in Table XX. The intensity ratios of three line pairs (see Table XXI) were related to the yttrium concentration in the usual manner. The analytical curves obtained from these line pairs are shown in Fig. 19.

During the past 2 years many comparisons of the results obtained from x-ray fluorescent and emission spectrometric methods have been made. The data shown in Table XXII are typical of the results of this comparison.

Table XX

Experimental Conditions for the Determination of Y_2O_3 in Rare Earth Ores and Concentrates

Spectrograph	Jarrell-Ash 3.4 meter Wadsworth grating spectrograph (15,000 rulings/inch grating)
Sample Electrode	1/2 inch diameter rotating disc electrode (National Carbon type L-4075) rotating at 10 rpm. Sample solution contained in gold dish (35 mm in dia. x 7 mm deep)
Counter Electrode	1 inch length of 1/8 in dia. graphite rod
Analytical Gap	4 mm
Excitation Source	National Spectrographic Laboratories "Spec Power" Model 110-2S, added capacitance: 0.0013 μ f Added inductance: 200 μ h Added resistance: 0 ohms Spark power setting: 7 Spark primary voltage Variac setting: approximately 60; adjust to give 7 breakdowns/half cycle (continued)

Table XX (continued)

Exposure Time	15 sec prespark plus 3 min exposure
Slit	45 microns
Emulsion	Eastman Kodak M plates
Filter	Corning #7740
Wave Length	3700-4300 Å second order
Intensity Modulation	Eight-step rotating sector
Emulsion	Two-step sector preliminary curve method using d.c. iron arc exposure

Table XXI

Analytical Line Pairs for the Determination
of Y_2O_3 in Rare-Earth Ores and Concentrates

Line Pair (Å)	Excitation Potential (ev)
Y 3982.60	9.8
Ce 3978.65	10.2
Y 3982.60	9.8
Ce 3984.675	10.6
Y 3982.60	9.8
Ce 3980.88	10.7

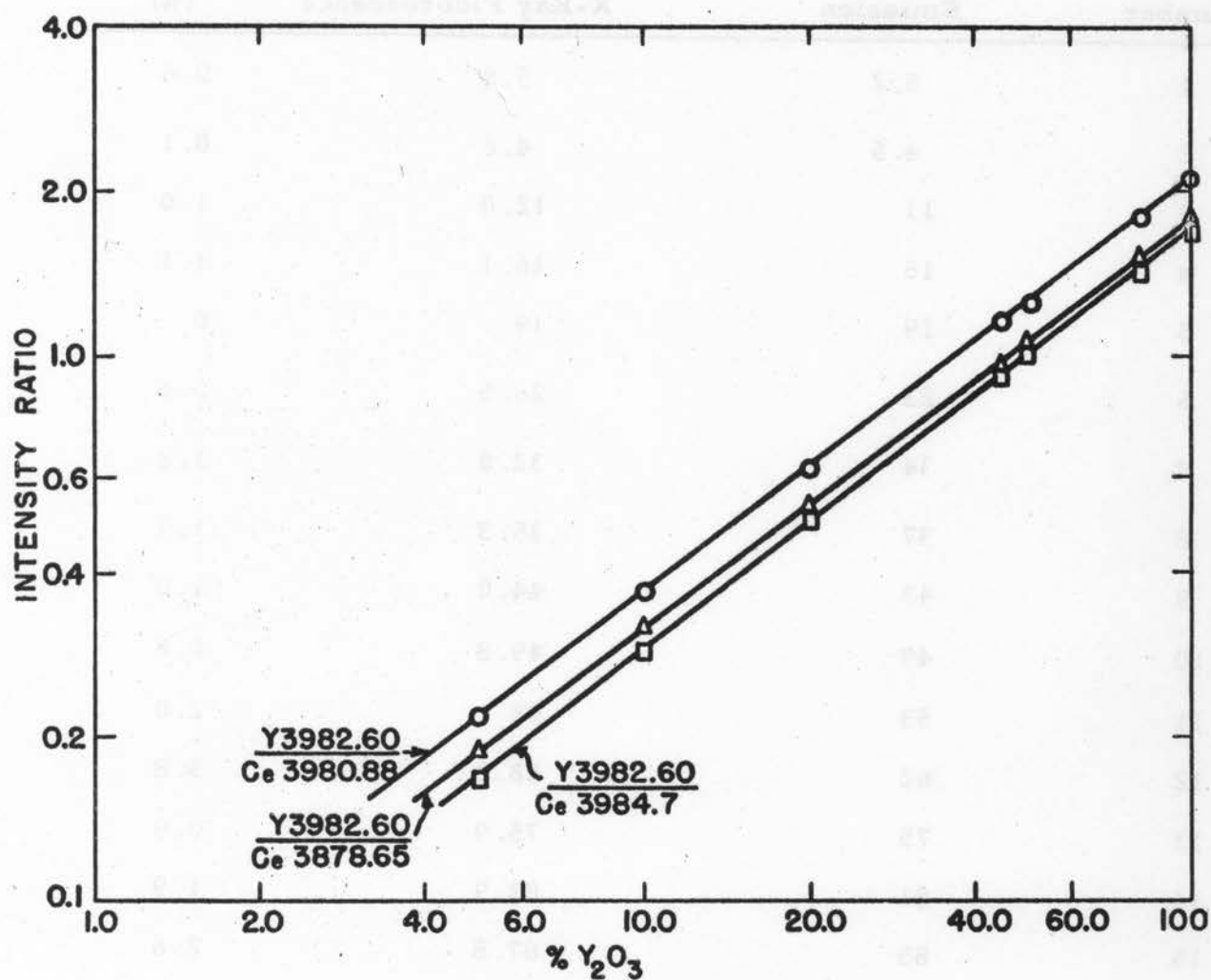


Fig. 19. Analytical Curve for the Determination of the Yttrium Content of Rare Earth Mixtures.

Table XXII

Comparison of X-Ray Fluorescent and Emission Spectrometric
Procedures for the Determination of Yttrium

Number	% Y_2O_3 Found		Difference (%)
	Emission	X-Ray Fluorescence	
1	5.2	5.8	0.6
2	4.5	4.6	0.1
3	11	12.0	1.0
4	15	16.1	1.1
5	19	19	0
6	23	26.5	3.5
7	34	32.8	1.2
8	37	35.3	1.7
9	43	44.0	1.0
10	49	49.8	0.8
11	53	55	2.0
12	62	58.2	3.8
13	75	75.9	0.9
14	81	82.9	1.9
15	85	87.8	2.8
16	90	91.0	1.0
17	92	93.7	1.7
18	99	98.4	0.6

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PART II. PROCESSING OF YTTRIUM ON A PILOT
PLANT SCALE

1. Historical Development of Yttrium Process

F. H. Spedding, O. N. Carlson and J. E. Powell

During the period of 1956-1958 the Ames Laboratory operated a rare-earth pilot plant for the production of yttrium metal for the U. S. Atomic Energy Commission. New and enlarged ion exchange columns, hydrofluorination furnaces, and metal producing equipment were constructed in the laboratory shops and assembled for use in this operation.

Over three thousand pounds of high purity Y_2O_3 were produced in the Ames Laboratory which in the early development and production stages served as the sole source of oxide for the metal process. A graphical plot of the monthly production rate of Y_2O_3 is presented in Fig. 20, showing the periodic effect of the two-month separation cycle.

As can be seen from the composite graph of Fig. 21 the amount of oxide produced in the Ames Laboratory was only a small fraction of the total oxide used in the metal process. As high purity oxide became available from commercial sources it too was used in this operation. The principal commercial supplier of the yttrium oxide

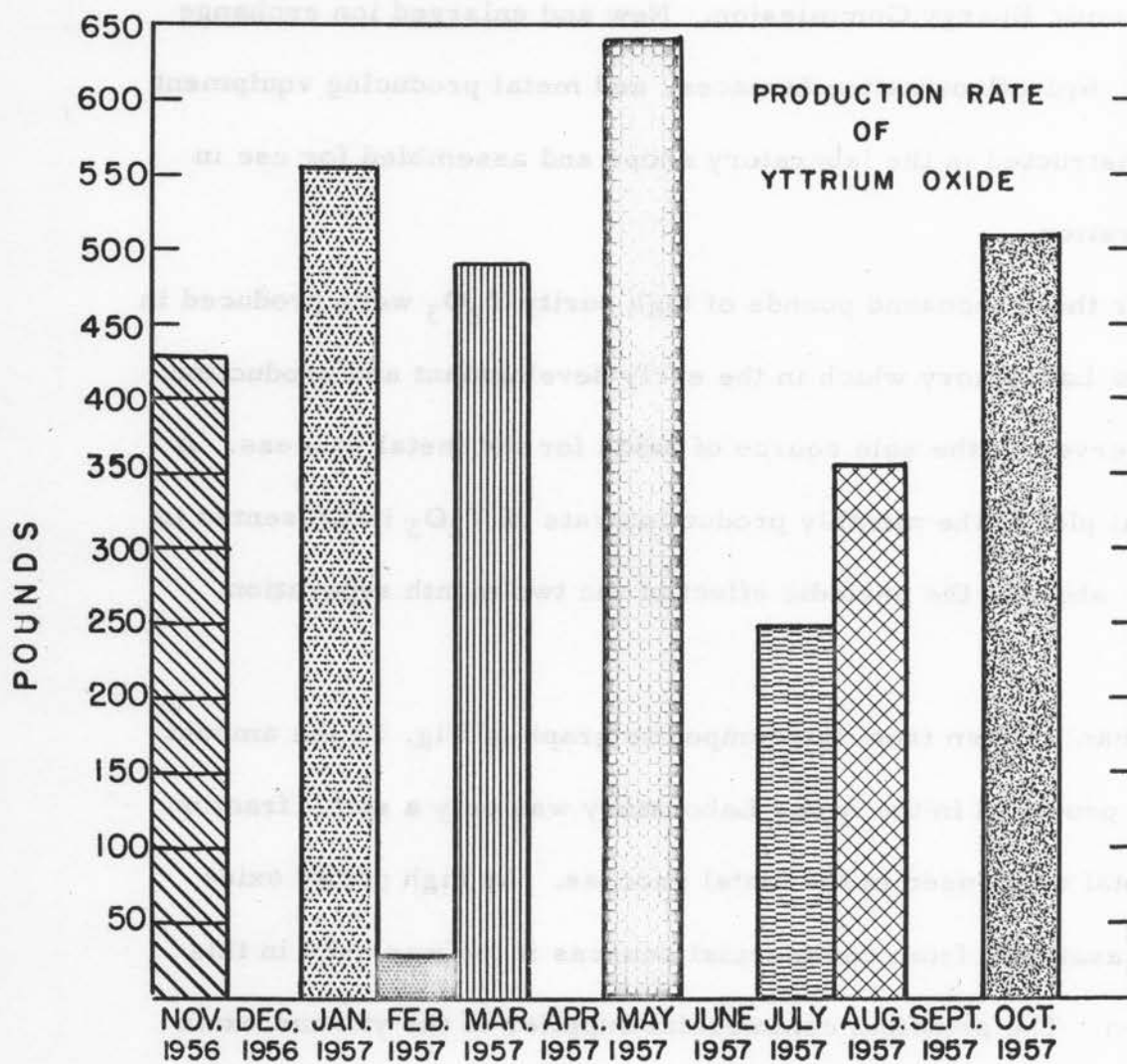


Fig. 20. Monthly Production of Yttrium Oxide at Ames during 1956-57.

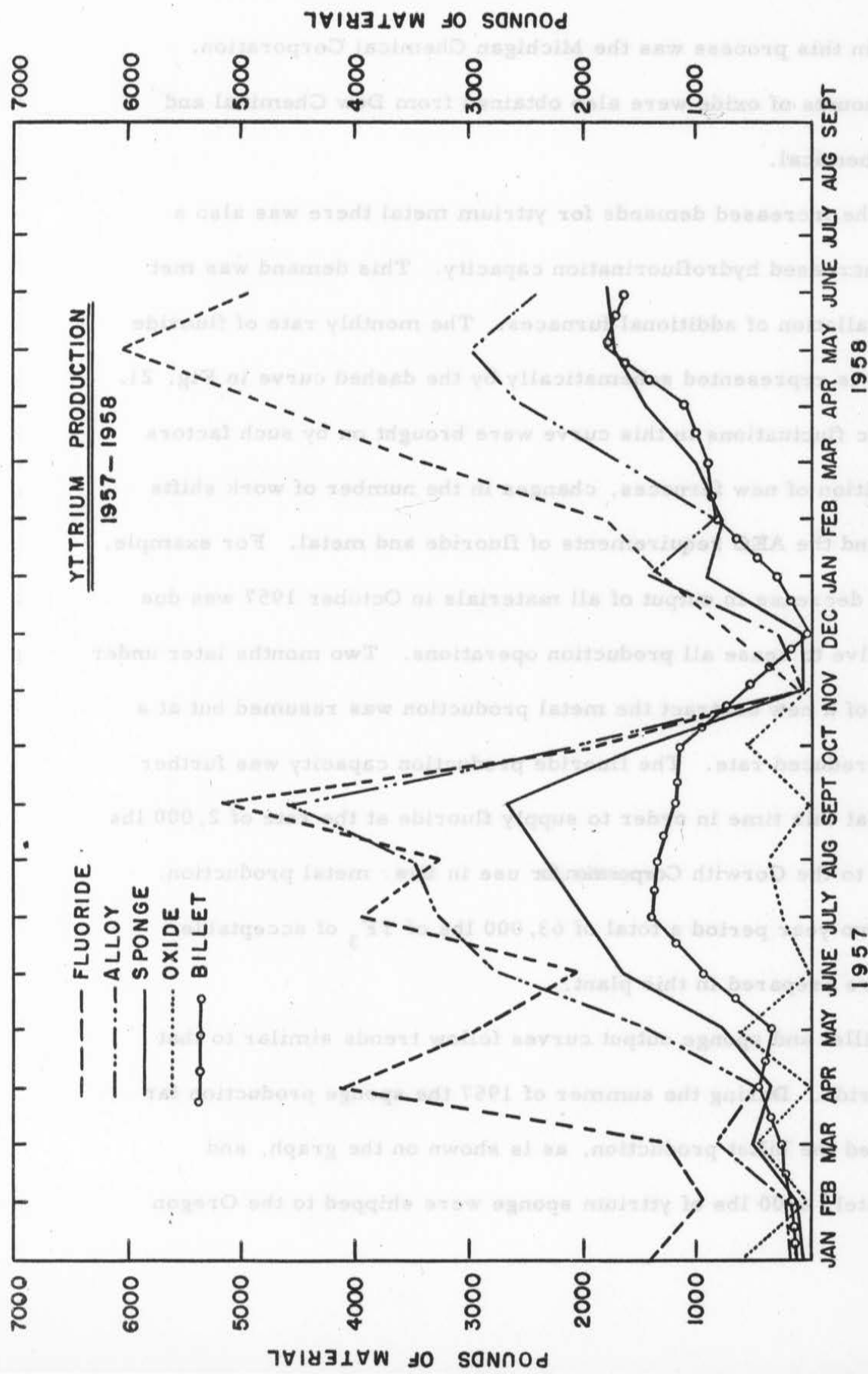


Fig. 21. Monthly Y_2O_3 , YF_3 and Y Metal Produced at Ames During 1957-58.

employed in this process was the Michigan Chemical Corporation. Lesser amounts of oxide were also obtained from Dow Chemical and Lindsay Chemical.

With the increased demands for yttrium metal there was also a need for increased hydrofluorination capacity. This demand was met by the installation of additional furnaces. The monthly rate of fluoride production is represented schematically by the dashed curve in Fig. 21. The erratic fluctuations in this curve were brought on by such factors as the addition of new furnaces, changes in the number of work shifts per day, and the AEC requirements of fluoride and metal. For example, the abrupt decrease in output of all materials in October 1957 was due to a directive to cease all production operations. Two months later under the terms of a new contract the metal production was resumed but at a somewhat reduced rate. The fluoride production capacity was further increased at this time in order to supply fluoride at the rate of 2,000 lbs per month to the Corwith Corporation for use in its metal production. Over the two year period a total of 63,000 lbs of YF_3 of acceptable quality were prepared in this plant.

The billet and sponge output curves follow trends similar to that of the fluoride. During the summer of 1957 the sponge production far outdistanced the billet production, as is shown on the graph, and approximately 4000 lbs of yttrium sponge were shipped to the Oregon

Metallurgical Corporation for arc melting. This was necessary because of the limited capacity of our arc melting facilities. A total of approximately 18,000 lbs of yttrium metal, in the form of billet or sponge, was produced and shipped to the Atomic Energy Commission during this period.

Representatives from various metal producing companies and laboratories visited the pilot plant and discussed hydrofluorination, reduction and melting techniques. This list included the following: Mallinckrodt, Michigan Chemical, Crane, Heavy Minerals, Albany Bureau of Mines, Wah Chang, Universal Cyclops and Lunex. Three engineers from the Crane Company, Mr. John Lenc, Irv Dzikowski and John Maher worked in the pilot plant during the first half of 1957. This arrangement was made at the request of the Atomic Energy Commission in order to expedite the industrial utilization of the know-how and techniques developed in this program at Ames as well as to alleviate the local man-power shortage brought on by the increase in production. Some of these men are now associated with the Corwith Corporation which employs the basic yttrium process described in this report.

2. Production of Yttrium Oxide

F. H. Spedding, J. E. Powell and H. Burkholder

2.1 Preparation and Loading of a Rare-Earth Solution

Digestion of xenotime sand was carried out in a 50-gallon, glass-lined, steam jacketed reaction vessel. The vessel was closed with provision for venting through a condenser and with water and air supply. The steam supply was passed through a gas super-heater to obtain the required temperature. A four hundred pound batch of 93% sulfuric acid was heated to about 190°C in the reactor. Two hundred and fifty pounds of finely pulverized xenotime, preheated to about 170°C, were then added to the reactor. The sulfuric acid-xenotime mixture was stirred by an anchor type agitator running at 100 rpm. The heat of reaction caused the temperature to rise slowly to 240-250°C and the reaction was nearly complete after 10-12 hours. The digested sludge was then flushed with cold water into a 300-gallon, glass-lined, storage and dilution tank and the reactor emptied with compressed air.

In order to load the first four columns of the ion-exchange unit with rare-earth mixture, it was necessary to digest seven 250-pound batches of xenotime in the manner described above. Each batch was

first diluted to 300-gallons and the strongly acidic initial solutions of rare-earth sulfates from all seven batches were filtered and passed through a small bed of anion-exchanger into the first and second columns of the cation-exchange unit. The undissolved rare-earth sulfates from each batch were allowed to accumulate in the dilution tank, and the combined material was finally leached repeatedly with water. The successive leachates became less and less acidic and were passed through the first and second columns as the third and fourth columns were loaded. In this way, an absorbed band of nearly neutral rare earths was obtained eventually which completely filled the first four resin beds. The excess rare earths were flushed out and recovered.

2.2 Elution and Recovery

Eleven 750-gallon stainless steel tanks were used for preparing and storing eluant (see Fig. 22). One centrally located storage tank was insulated and equipped with a steam heating coil and a thermostat for control of eluant temperatures. From this tank, eluant was cycled through a 50-gallon, constant head tank which supplied the ion-exchange unit.

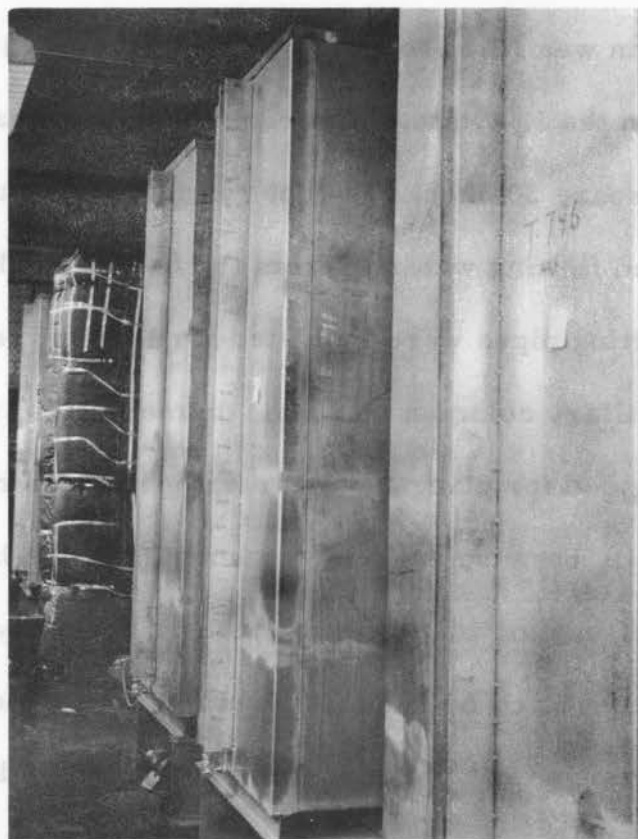


Fig. 22. Storage and Make-up Tanks for Eluant Solution.

An ion-exchange unit, constructed entirely of type 316 ELC stainless steel, was employed which was capable of processing the equivalent of 1000 pounds of R_2O_3 concentrate per cycle from 1750 pounds of xenotime. The main unit consisted of 12 columns, each 30 inches in diameter and 10 feet high. Each column was filled to the 9 1/2 foot level with 40-50 mesh Amberlite IR-120 in the H^+ -state. The resin beds were carefully backwashed by bolting a spare 30-inch x 10-foot cylinder to the top flanges of the columns and flowing water in from the bottom. These columns and their connecting pipes were insulated for the high temperature experiments. Three auxiliary columns the same diameter, but only four feet high, were also provided for diverting and storing various rare-earth fractions temporarily because sufficient quantities of the lanthanide elements are also present in xenotime to warrant their recovery. These auxiliary columns were connected by suitable plumbing to the older six-inch pilot plant. This arrangement not only made possible the direct, economical recovery of the less abundant rare-earth components, but also served to increase the yield of pure yttrium obtained per cycle. The ion-exchange units are pictured in Fig. 23.

The rare-earth band was eluted until it had advanced down the system the length of one column, or one-fourth of its own length. At that point, the front three-foot portion of the band was diverted to an auxiliary column



Fig. 23. Ion Exchange Units with Insulated Columns in Background and Auxiliary Columns in Foreground.

for further processing. This portion contained all of the rare earths heavier than dysprosium. After the band had moved six columns, or one and a half displacements, the rear part of the rare-earth band was cut off at the yttrium-terbium overlap and was left behind as the bulk of the yttrium was eluted on down the system. This was accomplished by moving the eluant feed tube forward. This part of the band was recycled each time the system was reloaded with fresh rare-earth mixture by coupling the columns in such a manner that the light rare earths from all previous runs immediately followed the new load. In this way, it was possible to allow the light rare earths to accumulate on the system, run after run, until it was practical to recover them as pure fractions.

When the band came off the ion-exchange system with the yttrium resolved, the product was collected in 100-gallon glass-lined tanks and precipitated as the oxalate. These tanks were equipped with a control system which filled the tanks consecutively and stirred the samples without constant attention. The supernatant solution was siphoned from the settled rare-earth oxalate precipitate and the residue was then washed from the collection tanks into large vacuum filters. These filters were constructed of stainless steel with perforated Bakelite bottoms. The vacuum was provided by means of steam aspirators.

The filtered oxalate was ignited to the oxide in fused quartz trays in electric muffles at 750-850°C (see Figs. 24 and 25).

In a total of six runs with this equipment, 3000 pounds of very pure Y_2O_3 were prepared and eventually converted to yttrium metal. Thus the Ames Laboratory performed a piece of needed research and at the same time provided the means to keep the program in yttrium metallurgy rolling at an ever increasing rate until commercial production of yttrium could meet the demand.



Fig. 24. Stainless Steel Filtering Units.



Fig. 24. Stainless Steel Filtering Units.



Fig. 25. Battery of Muffle Furnaces for Igniting Filtered Product to Y_2O_3 .

3. Production of Yttrium Fluoride

F. H. Spedding, O. N. Carlson and F. A. Schmidt

The next step in the yttrium metal process is the conversion of the oxide to the fluoride. The method that has been most successfully applied to the large scale required for this operation is the rotary bed furnace method. This combines a large production capacity with a consistency in the quality of the fluoride.

In this operation, fifty pounds of high purity yttrium oxide were placed in the inconel liner which was inserted into the outer inconel rotating tube. This loading step is shown photographically in Fig. 26. The tube was closed and the HF inlet lines connected to the system. Figure 27 is a photograph of the entrance end of three furnaces as they appear at the start of a hydrofluorination run. When the temperature of the furnace reached 150°C, the HF gas was turned on and the temperature of the furnace gradually increased to 750°C. The heating time for this portion of the cycle was about ~~six~~ hours, during which time the furnace bed was held stationary. After the furnace had been at 750°C for an hour, the inconel tube was rotated for ~~five~~-minute periods at 10-minute intervals. This rotation cycle was continued for a two-hour period after which the furnace and HF gas flow were turned

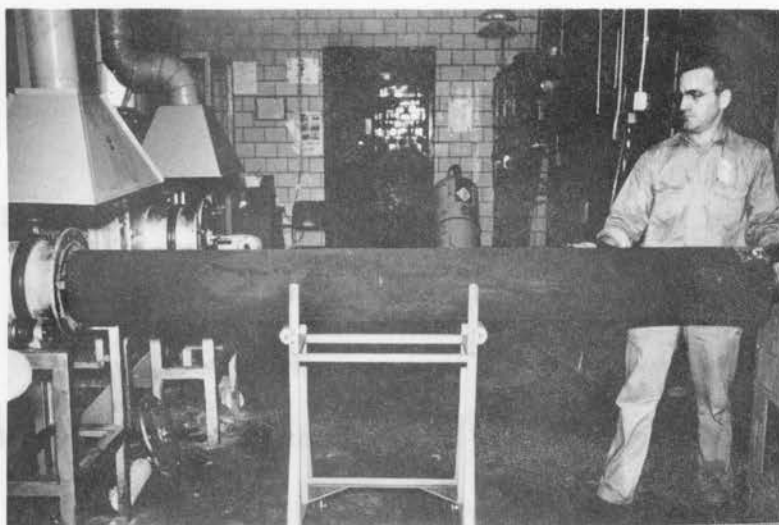


Fig. 26. Loading of the Inconel Liner Containing the Y_2O_3 into Rotary Tube Furnace.

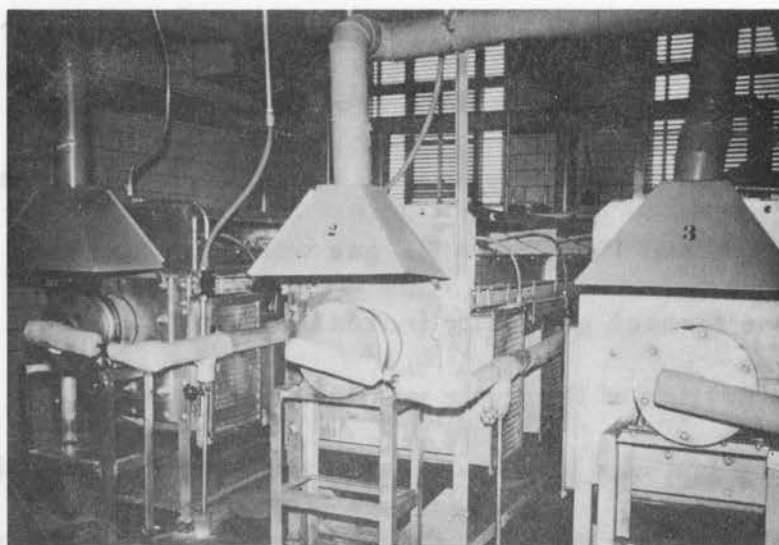


Fig. 27. Three of the Rotary Batch-type Hydrofluorinating Furnaces in Operation.

off. The fluoride was allowed to cool while in the furnace for 12 hours, usually overnight. The liner, containing the YF_3 , was then removed from the furnace and flushed with helium. After the fluoride had cooled to room temperature, the YF_3 was removed from the inconel liner in the manner shown in Fig. 28, evacuated, flushed, ground, sampled and stored in polyethelene bags in metal containers. Upon receipt of the analysis of the individual batches of fluoride, several batches were blended in a large tumbler-type mixer and stored in steel barrels ready for use in the reduction process. Those batches of fluoride with OIR values of greater than 0.45 were then given an additional hydrofluorination which reduced their oxygen content to an acceptable value.

For a period of several months, a single batch-type rotary furnace was used in the preparation of YF_3 . When the need for increased amounts of YF_3 for metal preparation was encountered, another furnace was constructed. When demand for fluoride was further increased, the fluoride operation was increased to two shifts per day. In order to run two shifts per day the tubes containing the fluoride had to be removed from the furnace while it was still hot ($400\text{--}500^\circ\text{C}$). The tubes were sealed and cooled to room temperature before unloading. The liners containing the oxide for the next



Fig. 28. Unloading the Liner Containing the YF_3 Product.

hydrofluorination run were therefore loaded into a hot furnace. With the two shift per day schedule it was noted that the number of batches of fluoride with intensity ratios above 0.45 was considerably higher than when a single shift was used. This is explained by the high temperature of the furnace at the beginning of the hydrofluorination cycle, causing sintering of the yttrium oxide, therefore making complete fluoride conversion more difficult. It also increases the possibility of the formation of YOF, due to the presence of a high concentration of vapor at temperatures above the pyrohydrolysis temperature of YF_3 .

Because it was not feasible to run two shifts per day in these furnaces, two additional rotary units were constructed in order to maintain the desired production level.

The yttrium oxide used as starting material came from three sources, Michigan Chemical, Dow Chemical, and the Ames Laboratory. A great deal of similarity in the hydrofluorination properties was noted between the Michigan Chemical oxide and the oxide prepared at the Ames Laboratory. They had similar packing densities and good conversion ratios were usually obtained during the HF treatments. However, using the above conditions, the fluffier, lower density Dow

Chemical oxide which is produced in a somewhat different way did not hydrofluorinate as well. It tended to form lumps and even after repeated hydrofluorination had OIR values of greater than 0.5. It is assumed that an acceptable quality of fluoride can be prepared from the Dow oxide although different hydrofluorination conditions will probably be required.

It has been observed that the amount of draft over the fluoride bed produced by the exhaust blower during hydrofluorination is quite critical. This draft is required to insure an adequate sweep of HF gas over the salt. When a decrease in the draft occurred (caused by the corrosion of the blades in the booster blower, wearing of the universal teflon seals, or partial line plugging due to accumulation of dust) a decrease in the quality of the fluoride resulted. As a result, manometers were installed in all of the HF inlet lines. These manometers contained the polymerized oil, Kel-F, which was used as the indicating fluid (density 1.8 g/cc). A draft of 4.0 - 6.0 cm was drawn on the units prior to turning on the HF gas and was maintained at approximately 1 cm of negative Kel-F pressure under gas flow conditions. An excess of HF of approximately 300% over the stoichiometric amount was used for each batch of fluoride. Fluoride prepared with the controlled draft and high excess of HF has a higher

per cent conversion. Approximately 80% of the batches of YF_3 prepared had an intensity ratio below 0.45 after a single treatment. The remaining 20% were given a second HF treatment which brought their OIR values below 0.45.

4. Calcium Redistillation

O. N. Carlson and J. A. Haefling

High purity calcium metal is an essential ingredient in the yttrium reduction process. As was pointed out earlier in this report, calcium reacts with atmospheric moisture forming an oxide or hydroxide film on the surface of the metal particles. This is particularly evident with granular calcium, but likewise occurs, though to a lesser extent, with the massive pieces. For these reasons, nearly all of the calcium metal employed in this work was redistilled at the Ames Laboratory. The calcium redistillation unit was originally constructed for purifying calcium which was used as the reductant in the thorium metal process, several thousand pounds of which were produced by the Laboratory in 1950-52. In this unit, 200 lbs of commercial grade, crude calcium can be vacuum redistilled in a single operation. A schematic drawing of the floor plan and equipment layout of the unit is shown in Fig. 29. A brick-lined, gas-fired furnace is recessed in a pit in the floor. Two identical vacuum units with redistillation retorts supported from the frame are lowered and raised by means of a pneumatic automobile hoist. Thus a single furnace serves for two distillation systems which are run on alternate days.

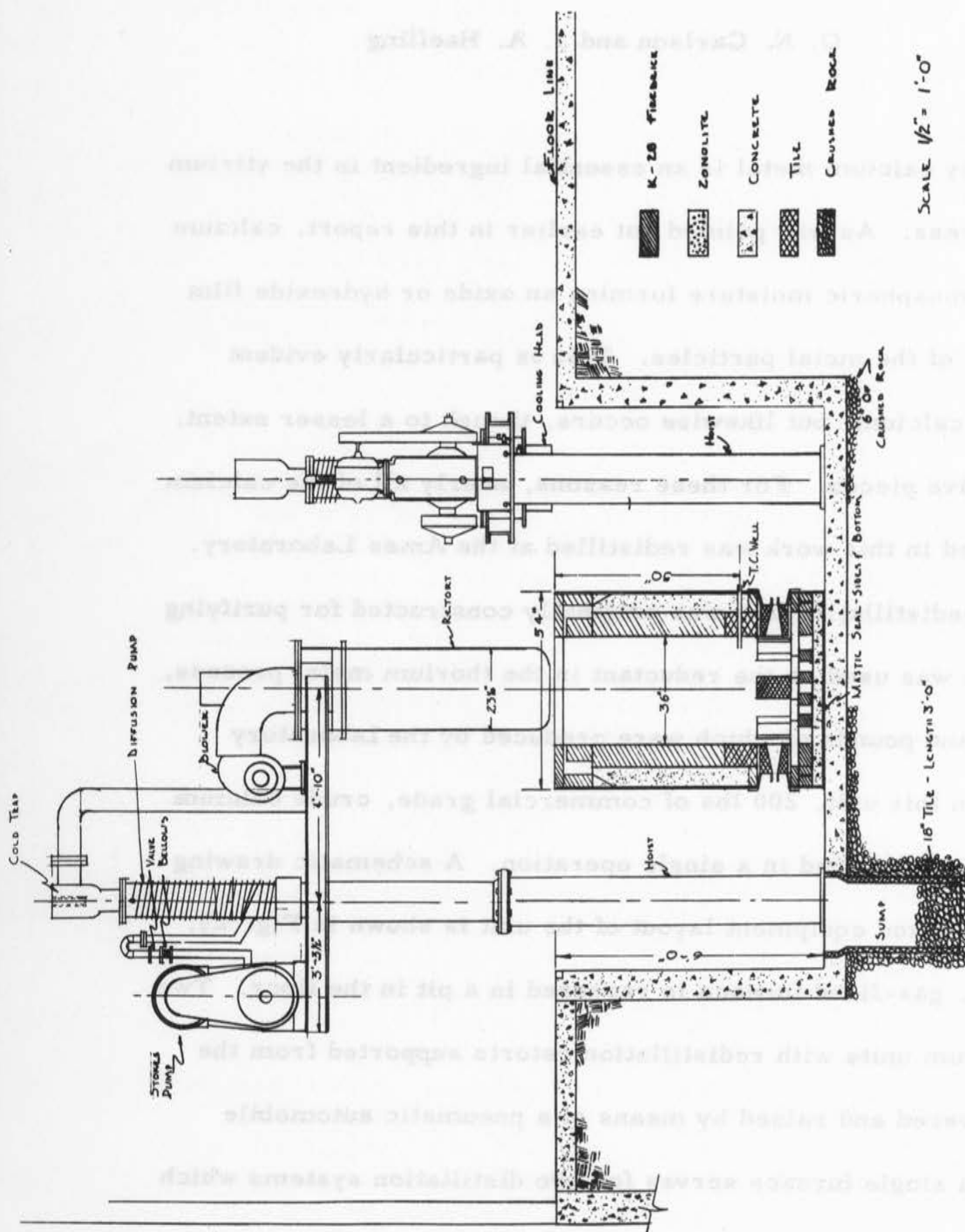


Fig. 29. Schematic Drawing of Complete Calcium Distillation Unit

The starting material for the distillation was commercial grade calcium metal obtained from the New England Lime Co. The principal impurities of this material are; aluminum, (0.1 w/o), magnesium (0.3 w/o), nitrogen (0.1 w/o), manganese (0.05 w/o) and oxygen (greater than 0.3 w/o). The crude calcium was loaded into a 310 Cb-stabilized stainless steel retort which was evacuated to a pressure of less than five microns. A photograph of the distillation retort is shown in Fig. 30. The distillation was carried out at a temperature of 900-925°C and the calcium vapors were condensed on an air-cooled condenser at the upper end of the retort. The temperature of the condenser was maintained at $300^{\circ}\text{C} \pm 50^{\circ}\text{C}$ during the distillation. The average rate of distillation in this system was about 25 lbs per hour.

At the conclusion of a run, the retort was raised from the furnace and lowered into a pit where it was allowed to cool, usually overnight. The system was opened and the condenser with the calcium "head" attached was raised from the retort. The condensate was quickly separated from the condenser surface by means of a chisel and stored in a tight container. All impurities, with the exception of magnesium, are virtually removed by the distillation. A representative analysis of the redistilled calcium is as follows: aluminum (0.003 w/o), magnesium (0.3 w/o), nitrogen (0.005 w/o), manganese (0.002 w/o), and oxygen (0.03 w/o).

The starting material for the distillation was commercial grade calcium metal obtained from the New England Lime Co. The principal impurities of this material are: aluminum (0.1 w/o), magnesium (0.3 w/o), nitrogen (0.1 w/o), manganese (0.05 w/o) and oxygen (greater than 0.3 w/o). The crude calcium was loaded into a 310 Cp-stainless stainless steel retort which was evacuated to a pressure of less

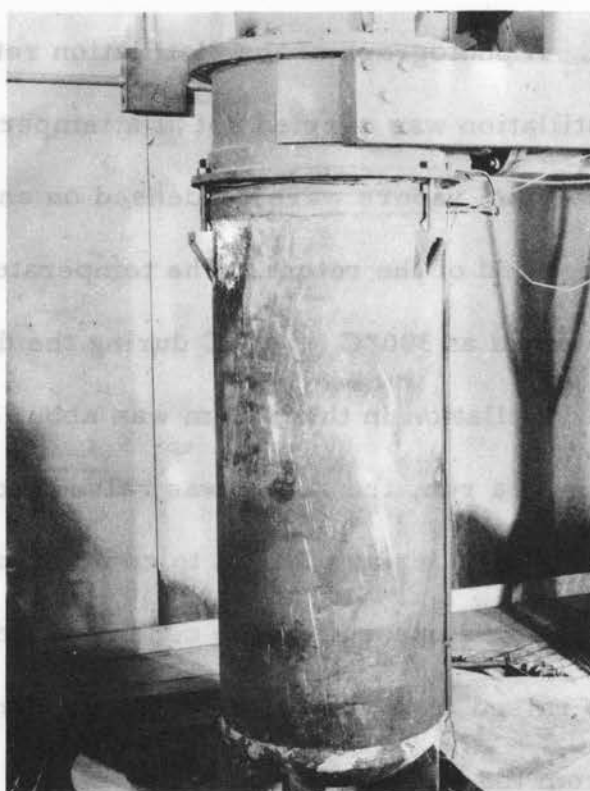


Fig. 30. Photograph of Stainless Steel Distillation Retort and Air-cooled Condenser.

and stored in a tight container. All impurities, with the exception of magnesium, are very low. A representative analysis of the redistilled calcium is as follows: aluminum (0.003 w/o), magnesium (0.3 w/o), nitrogen (0.005 w/o), manganese (0.005 w/o) and oxygen (0.03 w/o).

Because of the known reactivity of calcium toward atmospheric moisture, a special dry room was constructed adjacent to the furnace area. The relative humidity of this room was maintained at less than 20%. In this area the calcium heads were broken apart, weighed, ground and screened. For the reductions employing massive calcium, the distilled heads were broken on a hydraulic press into pieces weighing approximately 30 lbs. These were packaged in sealed metal containers for use in the reduction step. Figure 31 shows some of the pieces of calcium on the weighing platform of a scale. Other equipment which is sometimes used in the subsequent punching and grinding operations can be seen in the background.

The same equipment and very similar procedures were used in the redistillation of magnesium metal.

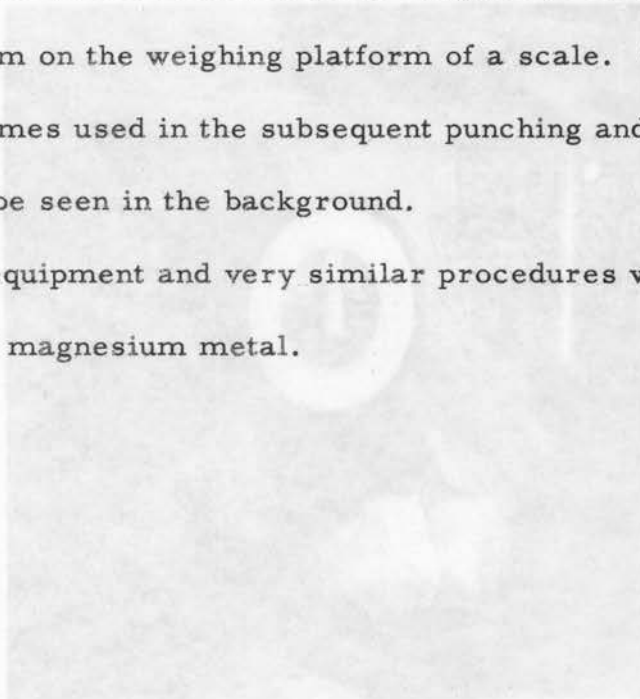


Fig. 31. Redistilled Calcium Metal on Platform of Scale.



Fig. 31. Redistilled Calcium Metal on Platform of Scale.

5. Preparation of Yttrium-Magnesium Alloy on a Large Scale

F. H. Spedding, O. N. Carlson, J. A. Haeffling
and F. A. Schmidt

5.1 Equipment Design and Construction

The design, construction and maintenance of the reduction pot is of crucial importance to the success of the reduction operation. Reactor grade zirconium or titanium ingots were rolled into plates, 48" x 96" x 1/4", by a commercial fabricator. The plates were then cold formed into cylinders 20-21" in diameter by 48" high. A flat disc cut from the remainder of the plate was welded into the bottom. A heliarc welding technique was employed in the welding of the bottom and side seam of the vessel. This was carried out in a shielded helium atmosphere using a "back-up" plate.

The titanium pot was surrounded by a steel jacket of 3/16" wall thickness, and a 1/2" thick graphite disc separated the steel and titanium on the bottom. The zirconium vessels were similar in design, but in these a thin titanium sheet (.032" in thickness) was used as a barrier between the zirconium and the steel jacket to prevent alloying of these metals at the reduction temperature. Handles were

welded to the steel jacket and tapped to fit 1/2" eyebolts for use in lifting. Figure 32 is a photograph of the reduction pot assembly including the outer steel supporting jacket and the lifting bar.

The reduction retort was constructed from a 24" diameter mild steel pipe with a 1/2" wall thickness and a length of 54 inches. A 3/4" plate was welded into the bottom. The top of the retort was cooled by a water jacket to protect a rubber gasket which made a vacuum seal between the retort and the head. The retort was lifted by means of a chain attached to the retort, enabling the entire unit to be lifted and transported by means of an electric hoist which was suspended from a monorail. The temperature of the retort was measured by chromel-alumel thermocouples, one of which was located in a well four inches from the bottom of the retort, and the second one twelve inches from the bottom. Because the retort was made of mild steel, it oxidized and scaled during the heating cycle. The average life of a retort was 20 runs, at the end of which time the lower two-thirds of the retort was cut off and a new bottom section welded on.

The vacuum head (Fig. 33) was designed with the following features: a sight glass, a 1" diameter vacuum port for a thermocouple probe, a six inch sliding vacuum valve to which the hopper is



Fig. 32. Zirconium Reduction Pot with Steel Jacket and Lifting Bar.

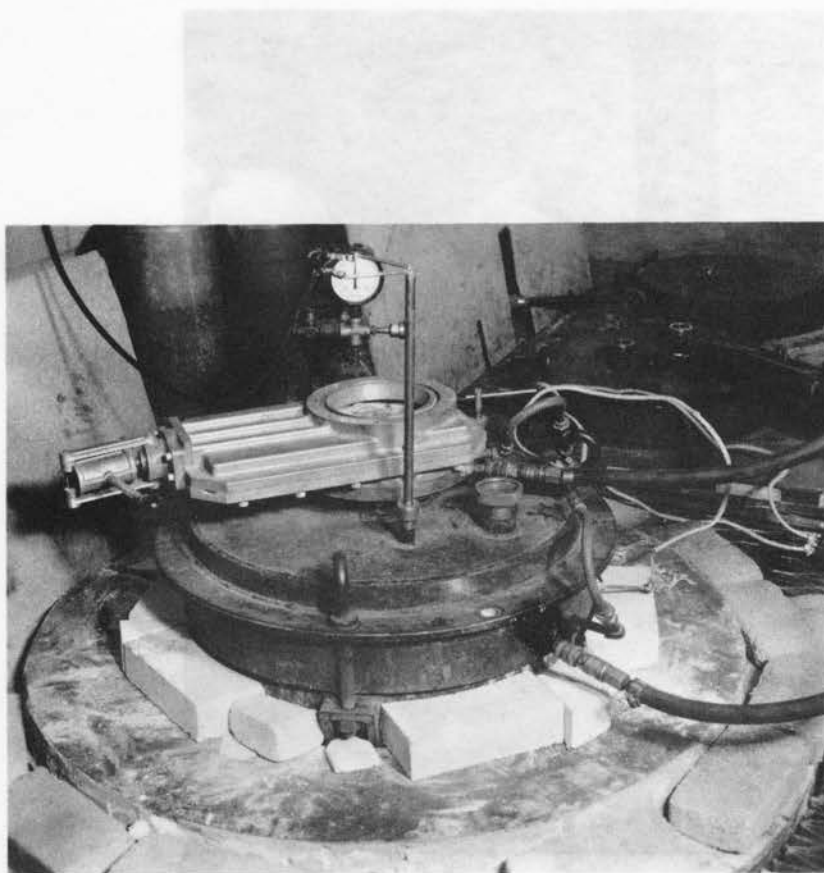


Fig. 33. Vacuum Head on Large Reduction Retort in Furnace Pit. Large sliding valve attached to head is visible in upper left. Thermocouple tube and sight glass are shown in center.

attached, and a flanged two-inch elbow connected to a vacuum line. The thermocouple probe consisted of a 1/2" diameter, stainless steel tube, the bottom section of which was covered by titanium tubing to protect it from attack by the molten slag and alloy. A compound vacuum-pressure gauge, a thermocouple vacuum gauge, and a toggle valve (which was used to release the pressure) were mounted on the vacuum outlet tube. A Stokes 212F Microvac mechanical pump was used to evacuate the retort.

The calcium chloride was dried in stainless steel containers which fit inside of a mild steel vacuum retort. This was heated in vacuo in a gas furnace to 450°C and the water vapors were pumped off and condensed in a dry ice-trichloroethylene cold trap. Upon cooling, the retort was filled with argon and the CaCl_2 container was quickly covered with a gas tight lid. The container was then jolted or tumbled to break up lumps which formed during drying. The transfer of the CaCl_2 from the drying vessel to an air tight storage bin is shown schematically in Fig. 34. The transfer was accomplished by means of a funnel which was placed over the drying vessel which was then inverted and hoisted to the top of the bin. The CaCl_2 was then poured through a sliding valve into the storage bin under an argon gas flow. Gas tight cover plates were bolted over both openings of the bin to insure complete exclusion of moisture during storage.

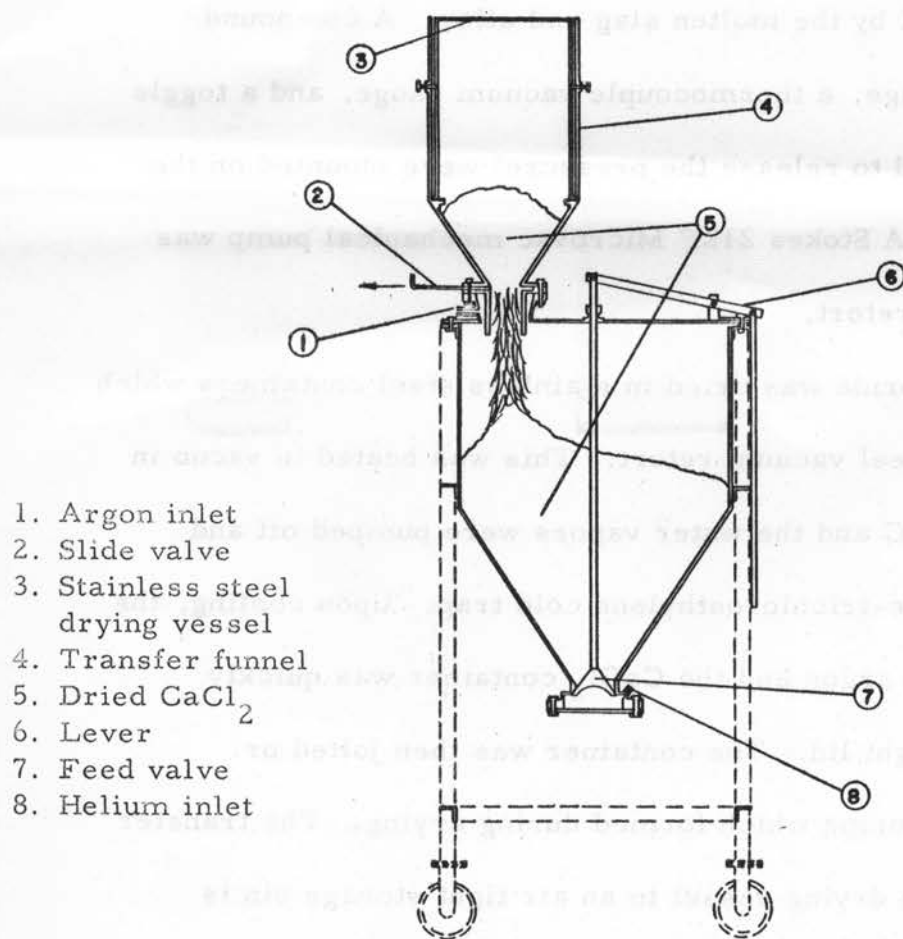
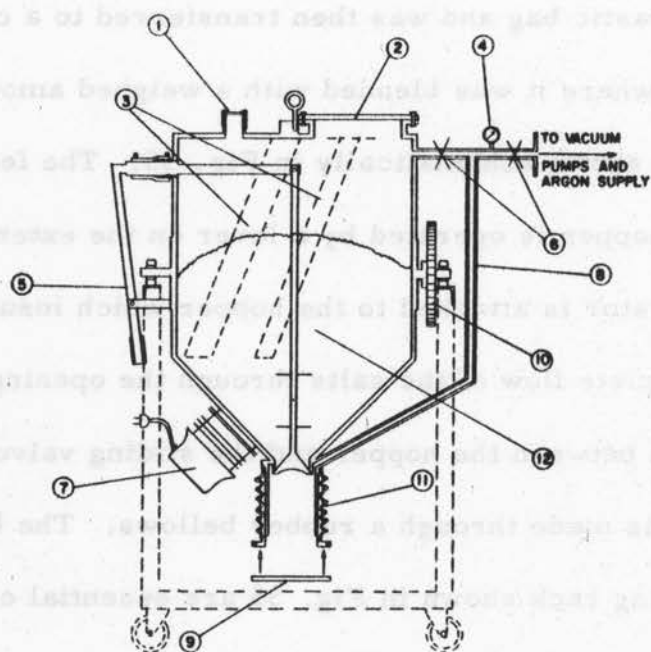


Fig. 34. Sketch of CaCl_2 Storage Bin and Transfer Funnel.

Weighing of the CaCl_2 and adding it to the reduction charge were carried out in the following manner. A polyethylene bag was placed over the flanged bottom and filled with helium gas and the conical valve within the storage bin was opened. The CaCl_2 was weighed directly into the plastic bag and was then transferred to a combination hopper and mixer where it was blended with a weighed amount of YF_3 . The hopper unit is shown schematically in Fig. 35. The feed valve in the bottom of the hopper is operated by a lever on the exterior of the apparatus. A vibrator is attached to the hopper which insures continued and complete flow of the salts through the opening. A vacuum connection between the hopper and the sliding valve on the head of the retort is made through a rubber bellows. The baffles, gears and supporting rack shown in Fig. 35 are essential components in the mixing operations.

Upon the completion of a reduction the hot retort was raised from the furnace and placed in a tilting rack. This device, made of angle iron, consists of a cradle which pivots on a supporting frame. The tilting mechanism for this apparatus is actuated by a compressed air piston which rotates the cradle and retort from a vertical to a nearly horizontal position.



- | | |
|--------------------------------------|--|
| 1. Sight port | 7. Vibrator |
| 2. Loading port | 8. Evacuation and flushing line |
| 3. Baffle plates | 9. Cover plate |
| 4. Pressure gauge | 10. Rotation gear |
| 5. Level for operation of feed valve | 11. Rubber bellows |
| 6. Vacuum valves | 12. YF_3 and CaCl_2 charge |

Fig. 35. Sketch of Feed Hopper Used for the Addition of YF_3 and CaCl_2 in the Large Scale Reductions.

5.2 Operating Procedure

The charge for a regular large scale reduction was as follows:

180.5 lbs of YF_3

163.0 lbs of CaCl_2

82.7 lbs of Ca (10% excess)

34.7 lbs of Mg (24% alloy)

The above charge yielded approximately 150 lbs of yttrium-magnesium alloy or 110 lbs of yttrium metal.

The calcium and magnesium were freshly distilled and in massive or chunk form as described in the preceding section of this report.

The calcium was placed in the bottom of the reduction vessel and the magnesium on top of the calcium.

The reduction vessel and its ingredients were then lowered into the retort, a titanium cover was placed over the vessel, and the vacuum head was fastened in place. The retort was evacuated to a pressure of below 100 microns. The retort, still under vacuum, was lowered into the hot, gas-fired furnace and pumping on the system was continued until the retort temperature reached 750°C . This usually required a heating period of 20 to 30 minutes. At this point the system was filled with helium to a pressure of 1 atmosphere.

Upon continued heating the expansion of the gas resulted in an increase in pressure which was released through a toggle valve, thus maintaining a positive pressure of less than 2 psi in the system.

After the calcium and magnesium in the reduction vessel had melted, the thermocouple probe was lowered into the melt. This was usually about three hours after the retort was placed in the furnace. In the meantime, weighed amounts of YF_3 and $CaCl_2$ were added to the hopper and blended. The hopper containing these ingredients was evacuated and back-filled with argon. The bottom plate was removed from the hopper, and the rubber bellows were attached to a sliding valve in the head of the retort, making a vacuum tight connection. The hopper and bellows were re-evacuated and filled with helium. A photograph of the apparatus at this stage of the process is shown in Fig. 36.

When the temperature of the melt reached $900^\circ C$, the vacuum valve (seen in the lower center of Fig. 36) was opened and the throat of the hopper was lowered through the valve opening by collapsing the rubber bellows. This feature was necessary to prevent the entrance of salt into the valve during transfer. The charge was added in small increments into the reduction vessel at a rate required to maintain the temperature of the melt above $800^\circ C$. The addition process generally required about three hours.

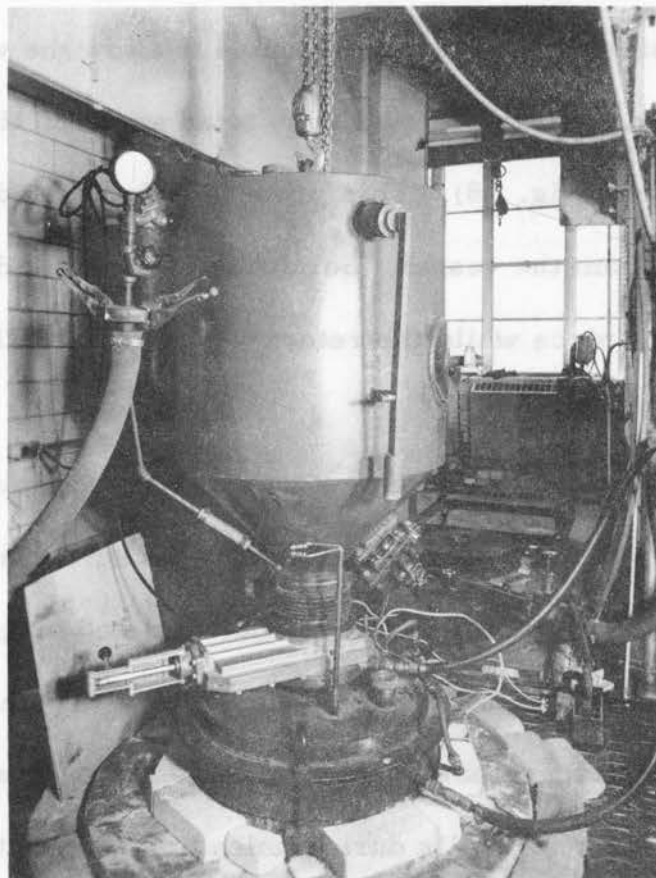


Fig. 36. Evacuation of Feed Hopper after being Connected to Vacuum Valve on Retort.

The retort was left in the furnace for another hour and one-half until the interior temperature reached 960°C . At this point the furnace temperature of the retort was generally between 1025 and 1050°C . At the conclusion of the run the hopper was raised, the vacuum valve closed, and the hopper disconnected from the retort.

The retort was lifted from the furnace (see Fig. 37) and transported by means of a monorail to the tilting cart. The retort was left in an upright position for about five minutes to allow the walls to cool somewhat, and then was tilted slowly to an angle of 15 to 20° from the horizontal (see Fig. 38). This procedure facilitated the removal of the alloy from the vessel. Solidification and cooling of the slag and alloy took place while the retort was in this reclining position.

After a 12-hour cooling period the retort was lowered into a pit, and hot water was run through the head and water jacket. This was done to prevent ignition of the finely divided calcium and magnesium condensate which collected on the head and upper parts of the retort during the reduction. If these parts were cold, moisture from the air would collect on the inner walls during unloading and ignite the metallic dust. Sometimes, especially when small amounts of sodium were present, the condensate ignited spontaneously upon exposure to



Fig. 37. Retort being Lifted from Furnace at Conclusion of Reduction.

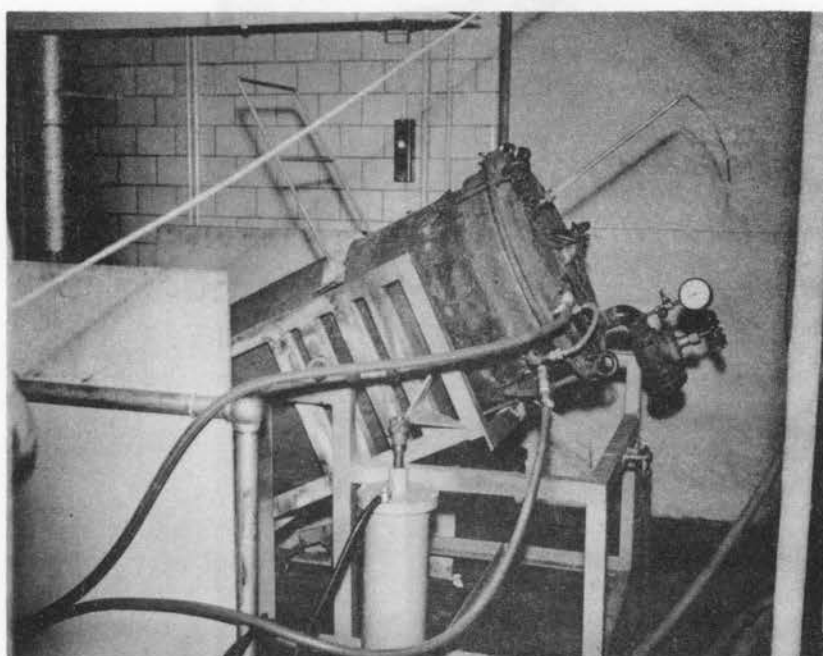


Fig. 38. Retort in Tilting Rack in Reclining Position during Solidification of Contents.

the air in spite of these precautions. The sodium was found to have come from sodium chloride present in some batches of CaCl_2 .

The slag was broken apart in the reduction vessel with an air hammer and removed. The alloy was then removed. This operation was carried out in a humidity controlled room. Sometimes the alloy came out easily and in one piece; at other times it adhered tightly to the reduction vessel, requiring considerable effort with an air hammer and chisel to break it loose. The relative volumes of the slag and the alloy from a large reduction can be seen from Fig. 39.

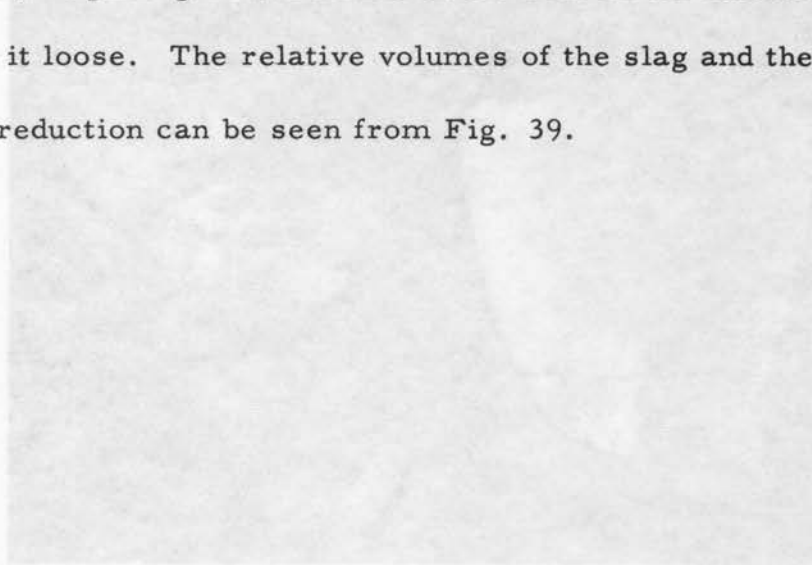


Fig. 39. Alloy (left) and Slag after Removal from Reduction Vessel.

The air in spite of these precautions. The sodium was found to have come from sodium chloride present in some batches of CaCl_2 . The slag was broken apart in the reduction vessel with an air hammer and removed. The alloy was then removed. This operation was carried out in a humidity controlled room. Sometimes the alloy came out easily and in one piece; at other times it adhered tightly to the reduction vessel.



Fig. 39. Alloy (left) and Slag after Removal from Reduction Vessel.

6. Removal of Magnesium by Vacuum Sublimation

O. N. Carlson, F. A. Schmidt and J. A. Haefling

The removal of the magnesium and the calcium, which is present in a small percentage, is accomplished by a vacuum sublimation step referred to as "demagging". This procedure produces a porous form of yttrium metal called "sponge". One of the principal problems encountered in this operation was the complete removal of the magnesium and calcium without melting the alloy. To accomplish this the alloy was crushed into pieces 1/2 inch in diameter or less and a carefully controlled heating schedule was followed during the sublimation step.

Because of its brittle nature, the alloy can be broken and crushed using conventional equipment. The massive alloy was first broken into chunks about the size of a man's fist, utilizing an electric hammer and chisel (see Fig. 40). Because of the slight pyrophoricity of the alloy, a jet of helium was impinged upon the point of the chisel during this operation. The alloy was then put through a large jaw crusher where it was crushed into pieces of approximately the size of golf balls. This was done in a Denver type-H jaw crusher obtained from the Denver Equipment Company. A protective shield was built around the crushing box so that a partial atmosphere of helium could be maintained during

Removal of Magnesium by Vacuum Sublimation

G. N. Carlson, E. A. Schmidt and J. A. Hurling

The removal of the magnesium and the calcium, which is present in a small quantity, is accomplished by a vacuum sublimation step referred to as "crushing". This procedure produces a porous

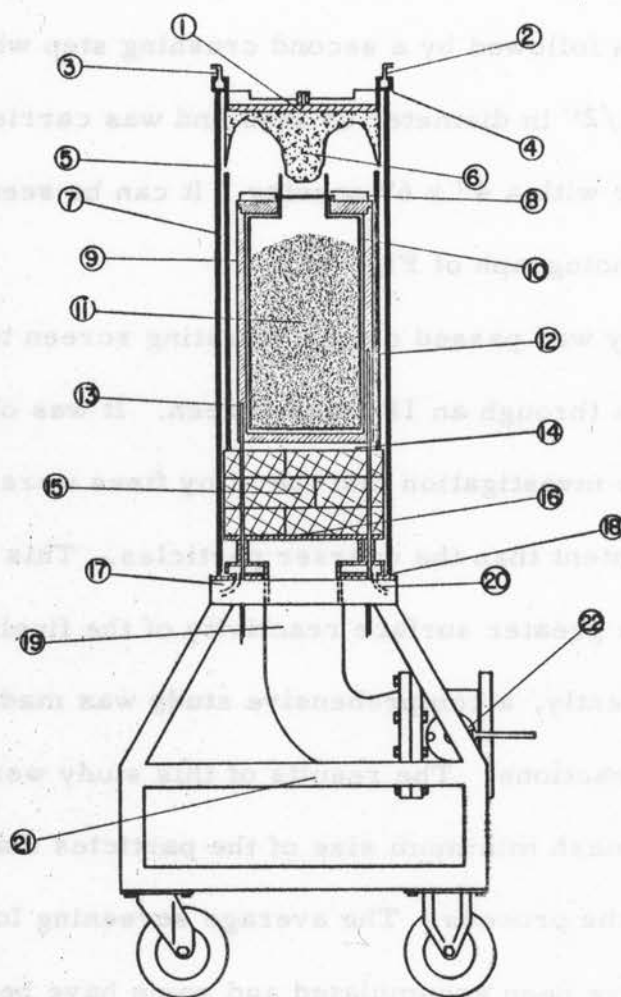


Fig. 40. Breaking of Alloy into Chunks during Crushing Step. Jawcrusher can be seen in background.

the operation. This eliminated sparking and burning of the fine metal particles. This was followed by a second crushing step which reduced the alloy to pieces $1/2$ " in diameter or less and was carried out in a smaller jaw crusher with a 4" x 6" opening. It can be seen in the background of the photograph of Fig. 40.

Finally the alloy was passed over a vibrating screen to remove those fines that pass through an 18-mesh screen. It was observed in the early part of the investigation that the alloy fines were much higher in oxygen content than the coarser particles. This was attributed primarily to a greater surface reactivity of the finely divided particles. Consequently, a comprehensive study was made on various screening fractions. The results of this study were used to establish the 18-mesh minimum size of the particles that should be carried on through the process. The average screening loss was 3-4%. The fines have been accumulated and some have been reprocessed back to the oxide as is described in a later section of this report.

The crushed alloy was then loaded into the demagging cart, a detailed sketch of which is shown in Fig. 41. The maximum capacity of this unit is 75 lbs of alloy. Since the reduction usually produced 130 to 150 lbs of alloy, the crushed alloy was divided into two equal portions and demagged in separate runs.



- | | |
|--------------------------------|---------------------------|
| 1. Condenser | 12. Thermocouple #1 |
| 2. Water jacket inlet | 13. Thermocouple #2 |
| 3. Water jacket outlet | 14. BeO insulation |
| 4. 1/8" Neoprene gasket | 15. K-30 insulation brick |
| 5. 14" I.D. quartz vacuum tube | 16. 1/16" copper plate |
| 6. Magnesium "head" | 17. Water jacket inlet |
| 7. 12" I.D. quartz sleeve | 18. 1/8" Neoprene gasket |
| 8. BeO insulation | 19. 6" vacuum line |
| 9. 10" I.D. graphite heater | 20. Water jacket outline |
| 10. 10" O.D. titanium crucible | 21. Furnace cart |
| 11. Yttrium sponge | 22. Valve |

Fig. 41. Schematic Drawing of Demagging Apparatus.

The demagging unit consisted of a vacuum base and cart and a graphite heater, inside of which was placed a titanium vessel containing the alloy. A quartz sleeve surrounded the graphite heater for insulation purposes and a quartz vacuum tube enclosed the entire assembly. A condenser head with a surrounding iron sleeve formed the vacuum closure on the upper end. The condenser surface was cooled by a stream of air which was propelled by a large fan. Heating was done by means of an induction coil powered by a 50 KW Ajax motor generator. The vacuum equipment consisted of a National Research Corp. B-107 oil booster pump backed by either a 212 CFM Kinney single stage mechanical pump or a 115 CFM Stokes Microvac pump. A pressure of less than 1 micron was maintained on the system throughout most of the run. A photograph of the entire apparatus including cooling fan, induction coil, quartz vacuum tube and vacuum system is shown in Fig. 42.

The following heating schedule was adhered to in order to assure maximum removal of Mg and Ca and still avoid melting and splattering of the alloy:

1. Heat to 750°C slowly over an 1 1/2 hour period;
2. Hold at 750°C for 3/4 hour;
3. Heat slowly to 1100°C at a rate of about 100°C per hour;

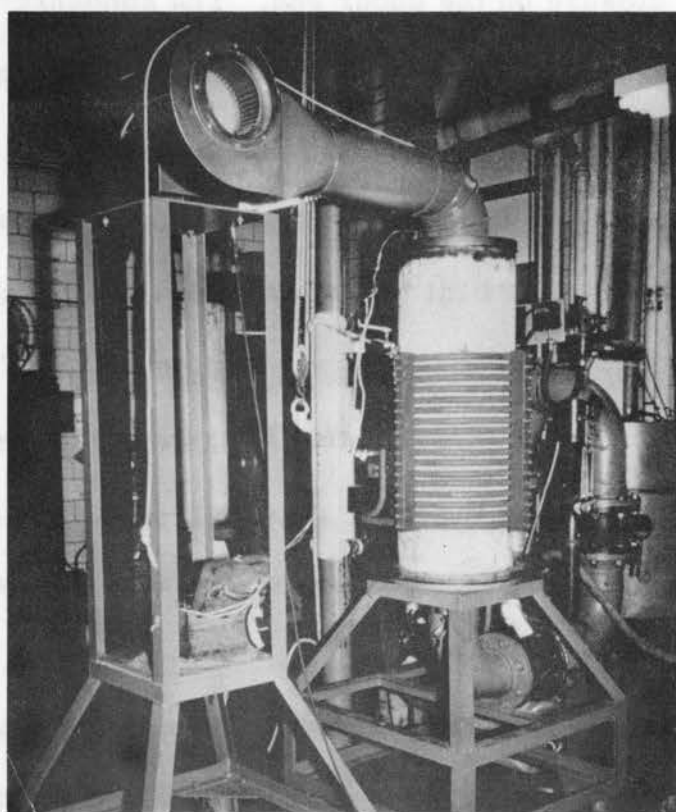


Fig. 42. Demagnetizing Unit Includes Cooling Fan and Condenser, Quartz Vacuum Envelope Surrounded by Induction Coil, and Portable Base.

4. Hold at 1100°C for 1 hour;
5. Heat slowly to 1200°C and maintain for 1 to 2 hours.

The contents were allowed to cool a minimum of 36 hours before opening. Attempts to unload the sponge while it was still slightly warm resulted, on one occasion, in a fire and complete loss of the sponge. A titanium vessel filled with sponge is shown in Fig. 43. A small pile of sponge can be seen in the center of the photograph and the condenser with the magnesium condensate still attached is shown in an inverted position at the left of the picture.

The residual calcium and magnesium in the sponge after the above treatment varied from 0.05 to 0.2%. The presence of too large amounts of these elements, however, was found to cause difficulty in the arc melting step resulting in an ingot with extremely rough sidewalls. It was observed that if the combined content of calcium and magnesium in the sponge was in excess of 0.05 w/o, difficulty was encountered in the arc melting operation. In order to assure consistently satisfactory removal of these volatile elements from the sponge it was necessary to resort to a second heating cycle. This was carried out in an apparatus similar to that used in the first cycle, but with twice the capacity. It consisted of a 14 inch diameter titanium pot, and a 19" diameter quartz tube. This unit was powered

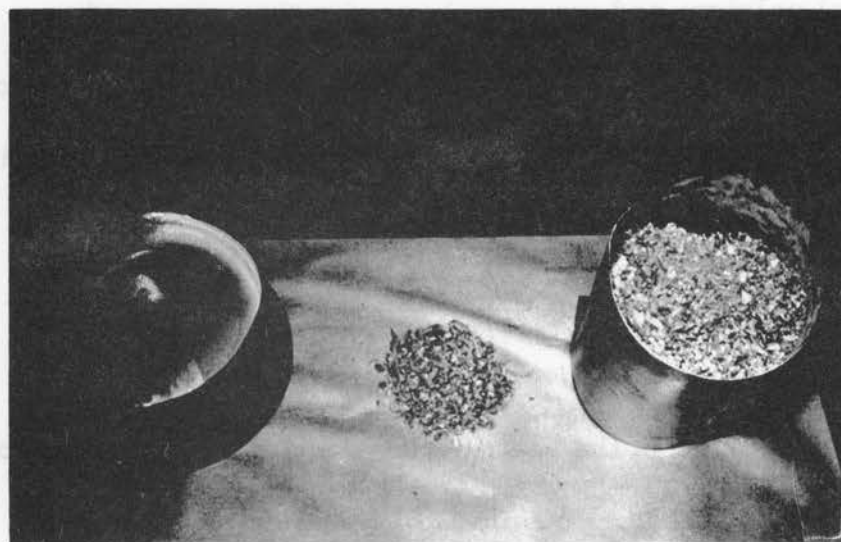


Fig. 43. Yttrium Sponge in Titanium Vessel (right) and Magnesium Condensate (left).

by a 100 KW motor generator. The sponge was brought quickly to 1200°C and held at that temperature for 5 or 6 hours. Since the amount of Ca and Mg removed was very small, no condenser was needed. The quartz tube employed in this operation had one closed end, and the Ca and Mg condensed on the walls as a thin film.

7. Arc-Melting of Yttrium Sponge

F. A. Schmidt and O. N. Carlson

The final consolidation of the sponge into a sound ingot was achieved by a double arc melting operation. In order to accomplish this efficiently, two consumable electrode arc furnaces were constructed, both furnaces operating alternately from the same bank of rectifiers. The yttrium sponge was compressed into compact form in a die (see Fig. 44) under a pressure of approximately 20,000 psi. The die was made of mild steel with a hardened steel plunger and hardened steel wearing plates on the inside surfaces of the die. The resulting bars or compacts, one of which is shown in Fig. 45, were 12" x 1 1/2" x 1 1/2" in size and weighed 3.3 lbs. Three compacts and an adapter were welded together in an inert atmosphere to form an electrode referred to as a "candle" (see Fig. 46). A short strip of high purity magnesium ribbon inserted in the end of the candle served as a fuse to assist in striking the arc.

The four-inch arc furnace, a detail drawing of which is presented in Fig. 47, consisted of a water-cooled copper mold into which the candles were consumably melted. The copper mold was surrounded

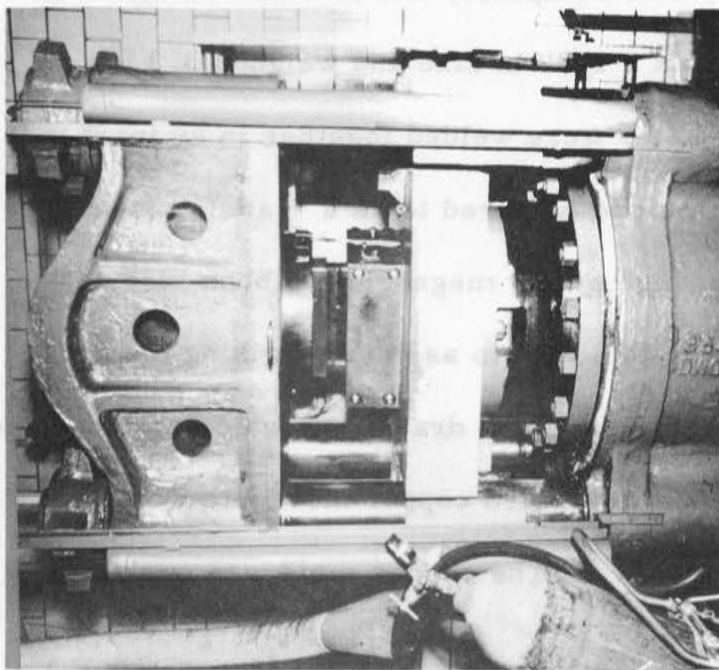


Fig 44. Die Assembly and Hydraulic Press
Used to Compact Yttrium Sponge.

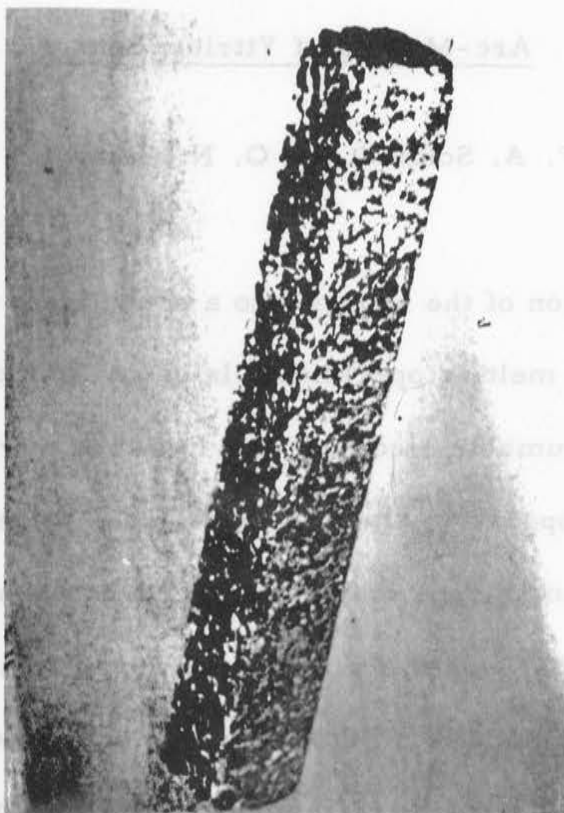


Fig. 45. Compacted Yttrium Bar.

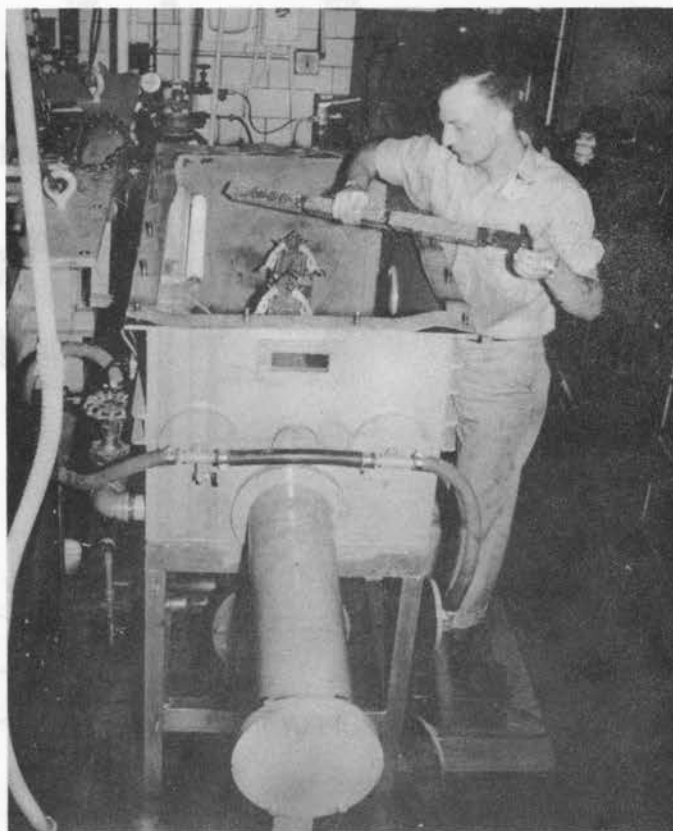


Fig. 46. Welding Box and Welded Electrode Used in First Arc Melting Step.

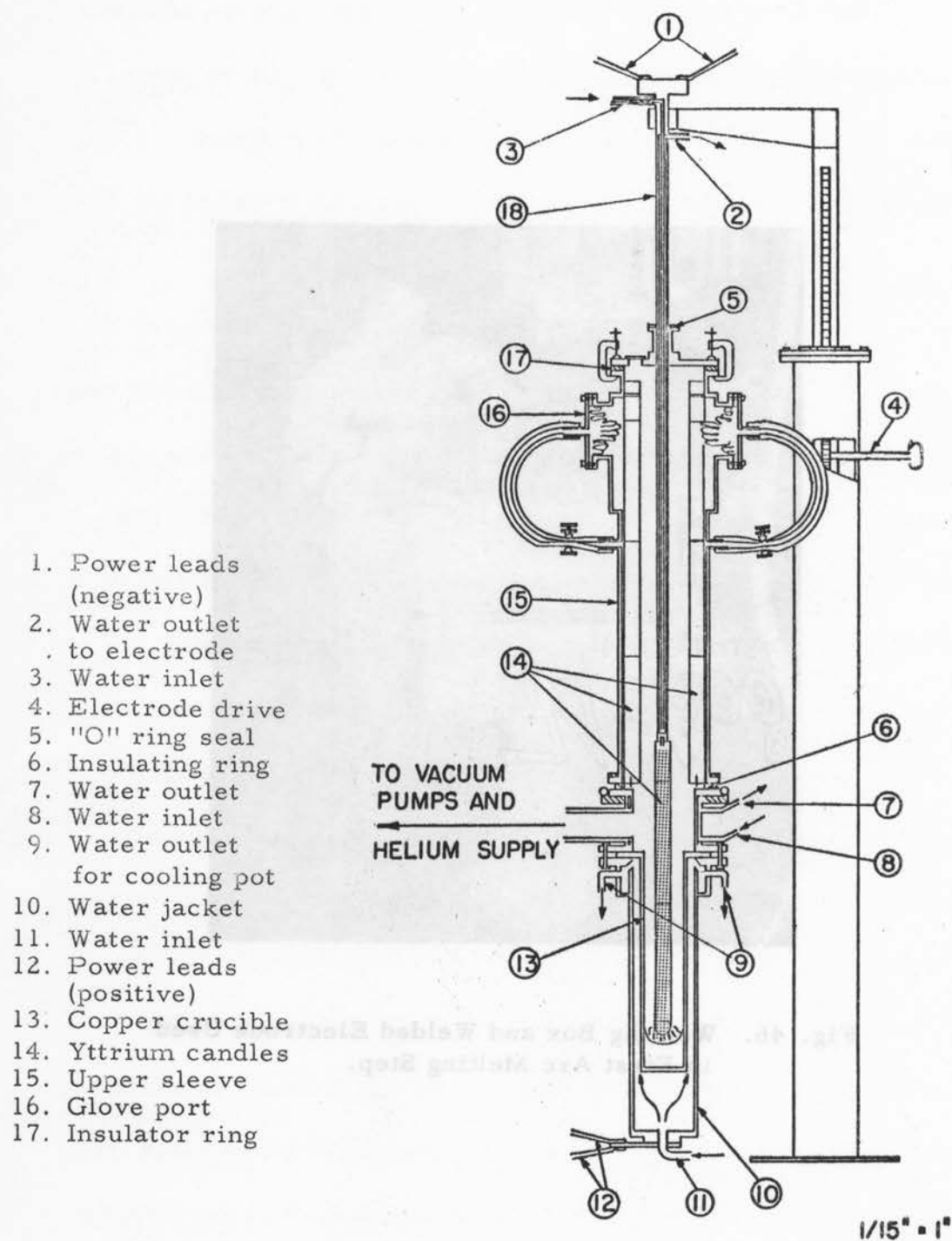


Fig. 47. Schematic Drawing of 4-Inch Diameter Arc Furnace.

by a water jacket. Approximately 10 gallons of water flowed through it per minute during the melting operation. The candles were attached to a movable copper ram which was also water cooled. Glove ports were used to remove the unmelted adapters and to attach fresh candles for melting. A photograph of this arc furnace is shown in Fig. 48.

In order to obtain the 4" diameter first melt ingot of sufficient length, one candle was attached to the water cooled copper ram and two were hung inside the upper chamber. An yttrium metal disc was placed in the bottom of the 4" copper mold and used as a striking pad. The furnace was evacuated to 10 microns and a leak rate taken. If the leak rate was less than one-half micron per minute, the unit was pressurized to 40-60 mm with helium gas and the melting operation started. This was done by lowering the energized electrode until the magnesium fuse came in contact with the yttrium pad. Once the arc was struck and the melting started, the power was kept constant by continually lowering the electrode. The power requirements for the first melt were 22-24 volts at 1000-1200 amperes. After the first candle was melted, the copper ram was raised and helium gas added until atmospheric pressure was reached. Through the glove ports the unmelted adapter was removed from the ram and placed in the disposal

by a water jacket. Approximately 10 gallons of water flowed through it per minute during the melting operation. The candles were attached to a movable copper ram which was also water cooled. Glove ports were used to remove the unmetallized slag and to attach fresh candles for melting. A photograph of this arc furnace is shown in

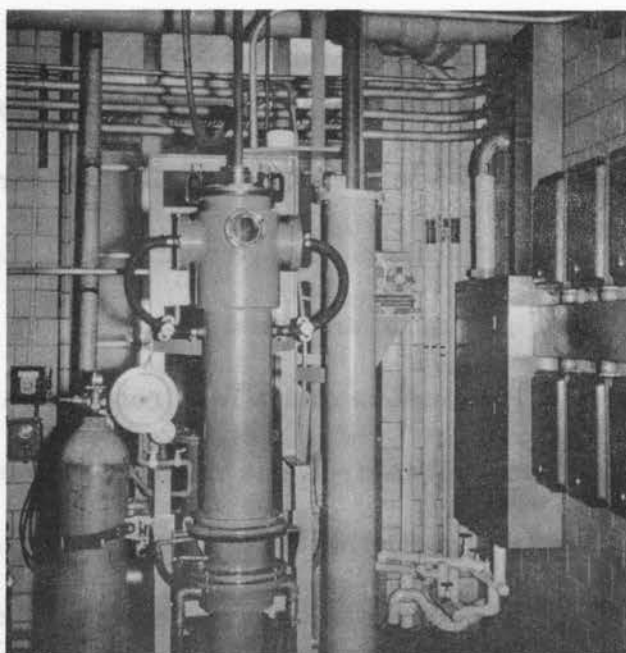


Fig. 48. 4-Inch Arc Furnace. Consumable electrode type.

continually lowering the electrode. The power requirements for the first melt were 21-24 volts at 1000-1200 amperes. After the first candle was melted, the copper ram was raised and helium gas added until atmospheric pressure was reached. Through the glove ports the unmetallized slag was removed from the ram and placed in the disposal

chamber located on the back side of the upper sleeve. The second candle was then attached to the ram and melted under a reduced helium pressure. The operation was repeated once more to melt the third candle. After one-half hour of cooling, the 4" ingot was removed from the mold and the striking pad and ingot crown cut off.

Three of these cropped ingots and an adapter were welded together in an inert atmosphere to form the electrode for the second melting step. The arc furnace which was used in the second or vacuum melting step is shown schematically in Fig. 49. It consisted of a 6" diameter, water-cooled copper mold which was surrounded by a copper water jacket. A flow of 30 gallons per minute of water was maintained during this melting operation. The water-cooled copper electrode was steel jacketed for reinforcement. Four water-cooled copper cables conducted the high current from the rectifiers. A dynamic vacuum of less than 20 microns was maintained on the system with a Stokes Model 212F pump.

Preparatory to melting, the 4" diameter electrode (approximately 60 inches in length) was screwed into the end of the copper ram. A small amount of yttrium sponge was placed in the bottom of the 6" mold on top of a half-inch-thick striking pad. The unit was sealed and

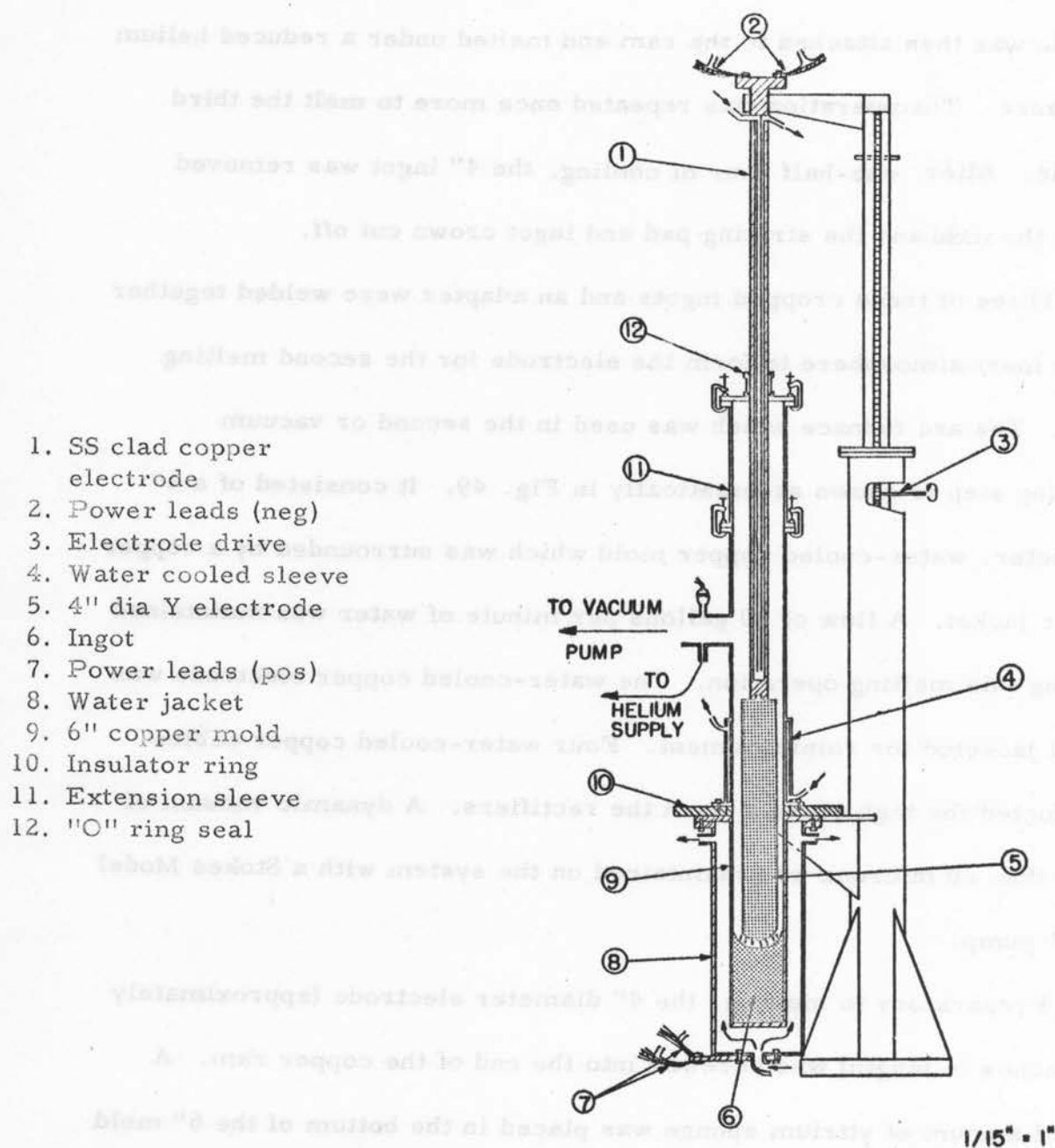


Fig. 49. Schematic Drawing of 6-Inch Vacuum Arc Furnace.

evacuated to 15 microns. The electrode was energized and lowered until it contacted the loosely packed sponge at which time the arc formed. The power required in this melting step was 20-24 volts at 2800-3200 amps which gave a melting rate of 4.5 pounds per minute. After melting, the ingot was allowed to cool for 1 hour and then removed from the copper mold. The striking pad and ingot crown were removed by a dry saw cut (see Fig. 50) and samples were taken for chemical analysis from a section machined from the top of the billet. Figure 51 shows compacts and four inch ingots together with a typical 6" vacuum-melted yttrium ingot weighing 85 lbs.

As previously mentioned in this report, the yttrium sponge after the first cycle of "demagging" contained between 500 to 2000 ppm calcium and approximately the same amounts of magnesium. These quantities were decreased to 350-500 ppm by a second demagging cycle. It was found that the condition of the sidewalls of the vacuum-melted 6" ingots depended upon the amount of these elements present in the sponge. For this reason, almost all of the sponge that was vacuum arc melted was doubly demagged. In this way the calcium and magnesium contents of the final ingot were decreased to less than 10 and 30 ppm, respectively.

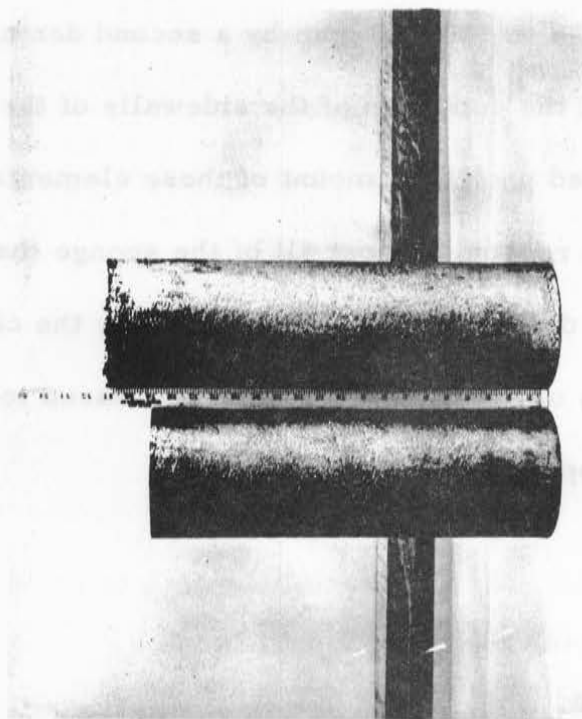


Fig. 50. Six-Inch Diameter Vacuum Arc-Cast Ingots before and after Cropping.

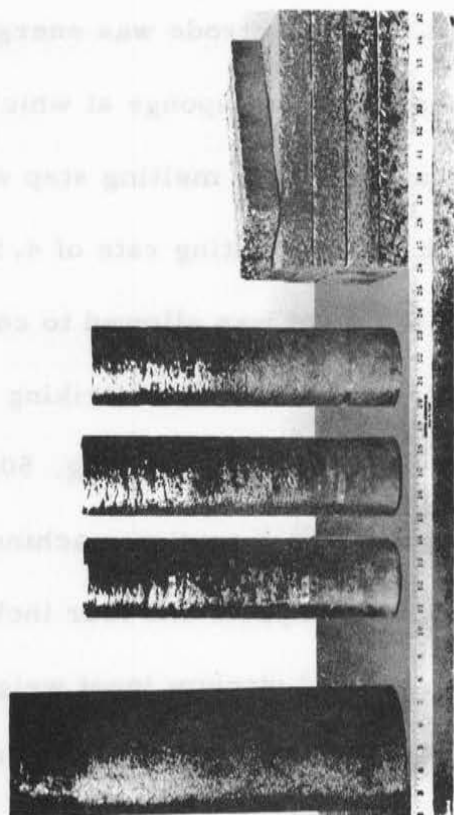


Fig. 51. 6" Vacuum-Melted Ingot, 4" Ingots and Compacts.

8. Large Scale Reduction in Tantalum Crucibles

A. H. Daane, C. E. Habermann and G. F. Wakefield

The preparation of yttrium by the reduction of yttrium fluoride with calcium in a tantalum crucible was scaled up to 10, and later, 16 pounds of metal per reduction, using the furnace described in Section 3.1 of this report (see Fig. 7). The tantalum reaction chamber for the 16 pound scale was 7" in diameter and 15" high; it required the use of the mold having the larger diameter slag chamber. The induction coil of this furnace was 15 1/2" in diameter and 30" high; it was powered by a 100 kw motor generator set, although at no time in the operation on this scale was a power input of greater than 50 KW required.

A typical series of runs on this scale of operation may be described as follows. The charge consisted of yttrium fluoride and a 3% excess of calcium over the stoichiometric amount required for the reaction:



This was mixed in a polyethylene bag and poured into the hopper. The whole furnace was then evacuated to 1 micron and heated to 1300°C to outgas the system. The furnace, including the hopper and mold, was then filled with argon purified by passage through a bed of hot calcium

granules, and heating was continued while the charge was added to the reaction chamber, which took about 20 minutes. A power input of 40 to 45 KW was required to keep the furnace at a temperature of 1500-1600°C.

The reaction between the YF_3 and the calcium was not violently exothermic at this temperature. As the molten reaction products settled into the two layers (the denser yttrium being on the bottom), more charge was added by operating the auger at a rate which prevented build-up and bridging of unreacted charge in the stack and the reaction chamber. The reaction chamber was then three-fourths full of molten metal and slag at a temperature of 1575° to 1600°C. At this point, the induction coil was lowered to include the focus inductor in the field. Five minutes of heating at a power input of 40 KW served to tap the melt. The draining of the reaction chamber could be seen through the translucent quartz tube. As this hot material entered the cool mold, the fluttering of the dead-weight gauge was another indication of the moment of pouring of the melt.

As soon as the melt was tapped, the 2" slide valve was closed, another charge was added to the hopper, and it was evacuated and equilibrated with the furnace atmosphere. About 30 minutes after pouring, the mold and contents had cooled enough so that the 4" slide valve

over the mold could be closed and the mold removed from the furnace. Much of the excess calcium in the reaction products condensed in a finely divided deposit around the top of the mold and was scratched with a rod to intentionally "flash off" this pyrophoric material in a quick burst of fire. The mold was then upended to deliver the slag and metal which were readily separated with a clean interface. The ingot usually contained a small slag pocket that was about 1" in diameter and several inches deep. This was drilled out to give a slag-free ingot. Several of these were welded together to give consumable electrodes for vacuum arc melting as described in the preceding section of this report. Because of the high calcium content of the ingots, difficulty was encountered in vacuum arc melting and the resulting arc-cast ingots had very irregular sidewalls.

It was found that six such melts could be run in an eight hour day, and in experimental runs a little more than 800 pounds of metal were prepared by this process. A typical analysis of an ingot from this process showed the following amounts of impurities in parts per million: Ca, 5000; Mg, 20; Si, 60; Ta, 4000; Ti, 3; Fe, 300; Cu, 60; N₂, 220; O₂, 2050 and C, 110. The calcium content could be lowered to less than 10 ppm in vacuum arc melting operations, but the tantalum content,

of course, remained unchanged. As described previously, by observing special precautions in smaller scale runs, it was possible to lower the oxygen content, and some of these same precautions could be utilized in work on this larger scale to achieve lower oxygen content metal, but at a significant loss in convenience and rate of operation.

9. Scrap Recovery

A. H. Daane, C. E. Habermann, R. W. Fisher and

D. Provow

In the metallurgical operations, a considerable quantity of yttrium scrap was accumulated in the form of billet croppings, heavy turnings, unused electrodes, etc., that was of satisfactory purity for further use. To recover this material in usable form, a scrap melting furnace was assembled that consisted of the tantalum crucible reduction furnace of Fig. 12, modified by eliminating the hopper and charge addition assembly on the furnace head, and using a tantalum crucible with a removable lid. Approximately 30 pounds of yttrium scrap could be melted in an argon atmosphere and tapped into the water cooled mold in each melt. The furnace required 8 to 10 hours to cool to room temperature after each melt, and since it had to be opened for recharging with scrap, only one melt could be made per day. This process added no significant amounts of impurities with the exception of tantalum. The tantalum pickup was particularly apparent when scrap metal from the magnesium alloy process was used. A little more than 400 pounds of scrap was recovered by this procedure.

A chemical process has been developed for the recovery of pure yttrium oxide from turnings, saw filings, and oxide dross containing

no rare earth impurities. This scrap was unsuitable for metallurgical operations because of its high oxide content and the presence of other metallic impurities. The details of the process are described in a recent report by D. Provow and R. W. Fisher.¹

The principal steps of the process are:

- 1 dissolution with a stoichiometric amount of nitric acid;
- 2 the precipitation of the hydroxide impurities at the end of the reaction by a 50% dilution of the solution to a pH of 4.5;
- 3 precipitation of copper and nickel with ferrocyanide; and
- 4 precipitation of yttrium oxalate with oxalic acid.

Approximatley 400 pounds of yttrium oxide were recovered in this manner in batches of 100 pounds.

The reaction was carried out in glass-lined tanks, but stainless steel can be used. The precipitation and filtration steps can be carried out in glass-lined, rubber or plastic lines, or stainless steel equipment.

The chemical cost of a large scale operation is 67 cents per pound of yttrium oxide and could be lowered by recycling the nitric and oxalic acids. The metallic impurities, zirconium, iron, titanium, nickel, calcium and magnesium were either not detected in the recovered oxide by spectrographic analysis or were less than 20 ppm.

References

- (1) D. Provow and R. W. Fisher, "Chemical Processing of Yttrium Scrap", U. S. Atomic Energy Commission Report ISC-1160 (1959).

10. Preparation of Low Oxygen Yttrium Metal

O. N. Carlson, F. A. Schmidt and J. A. Haeffling

Approximately 400 lbs of yttrium metal which were low in oxygen were produced in the early part of 1959, using the salt extraction technique discussed in Section 3.2 of this report. A regular large scale reduction was carried out in the manner described in a preceding section using a titanium reduction pot. After a cooling period, the slag was removed and fresh YF_3 and $CaCl_2$, in the weight ratio of 2:1, were added to the alloy in the reduction crucible. The amount of YF_3 employed in this step was about 50% of the amount of YF_3 used in the initial reduction. A stirrer, fabricated from steel tubing which was clad with titanium sheet, was inserted through a water cooled "O" ring universal seal in the vacuum head. The charge was reheated to $950^\circ C$ and stirred for one-half hour. The retort was allowed to cool in the tilting rack and the slag and alloy were removed from the pot in a low humidity room.

Crushing and screening of the alloy were carried out in a large steel chamber or dry box which was evacuated and then filled with helium. The chamber is 3 feet in diameter by 8 feet in length with

glove ports on both sides to enable the operator to carry out the desired operations in an atmosphere free of oxygen and water vapor. A photograph of this unit is shown in Fig. 52. The alloy was broken up with an electric hammer operated within the box and crushed in a small jaw crusher that had been installed in the chamber.

An important modification was made in the "demagging" process utilizing a long time, low temperature heating cycle. This eliminated the refractory and insulating materials that are required in the high temperature induction heating method discussed previously, and which are potential sources of oxygen and other adsorbed gases. It has the additional advantages of completely removing the magnesium and calcium from the sponge in a single treatment and of eliminating partial melting and sintering of the particles so often encountered in the higher temperature method. A unit capable of processing 100 lbs of alloy per batch was constructed and is shown, as assembled, in Fig. 53. The retort was fabricated from a 10" diameter stainless steel tube. This can be seen protruding from the Hevi-Duty resistance furnace. The crushed alloy was contained in a titanium vessel which was inserted into the retort. The furnace was heated electrically by nichrome heater elements and could be controlled to $\pm 2^{\circ}\text{C}$ at 950°C . The rack shown at the left of the photograph supports a blower which forces air onto the condenser,

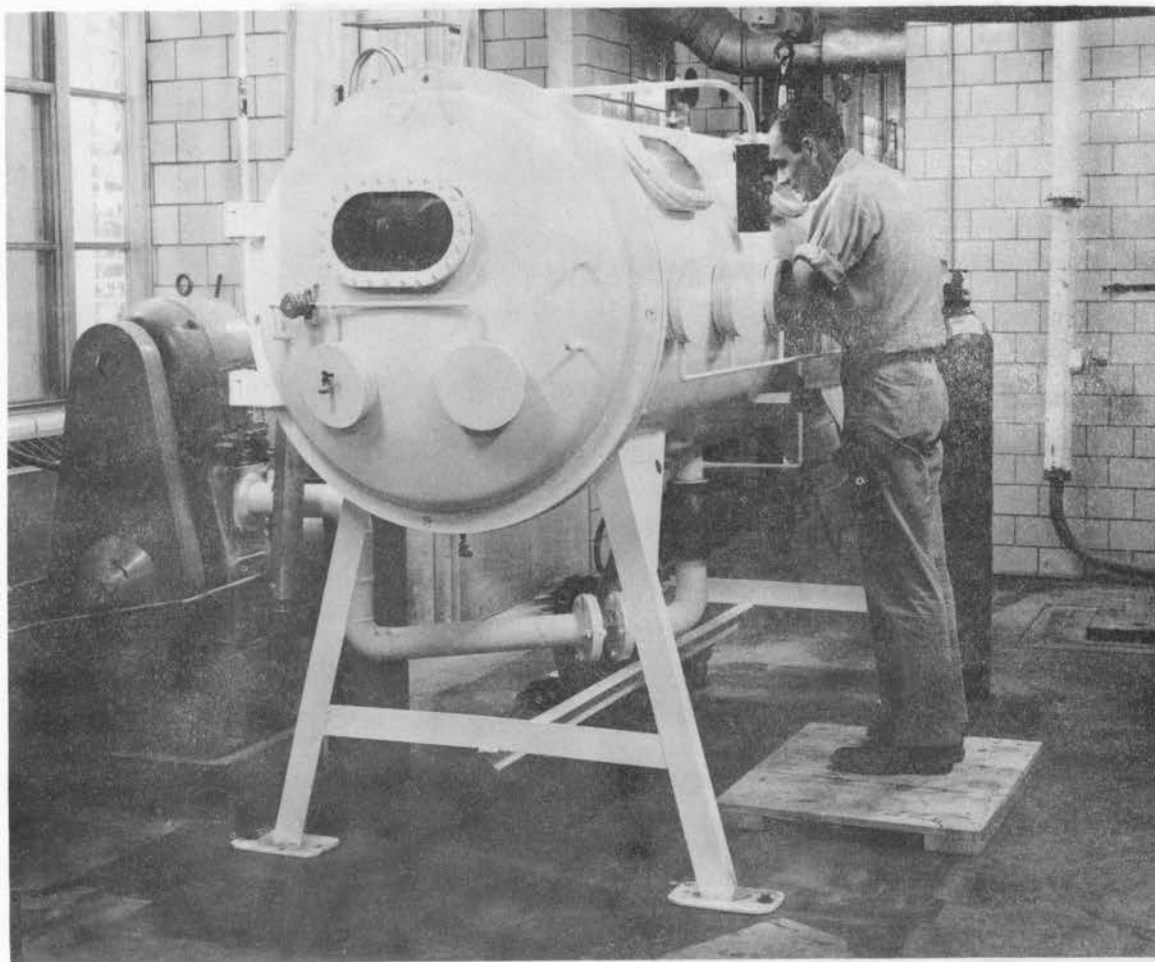


Fig. 52. Large Chamber Used for Handling and Crushing Alloy in an Inert Gas Atmosphere.

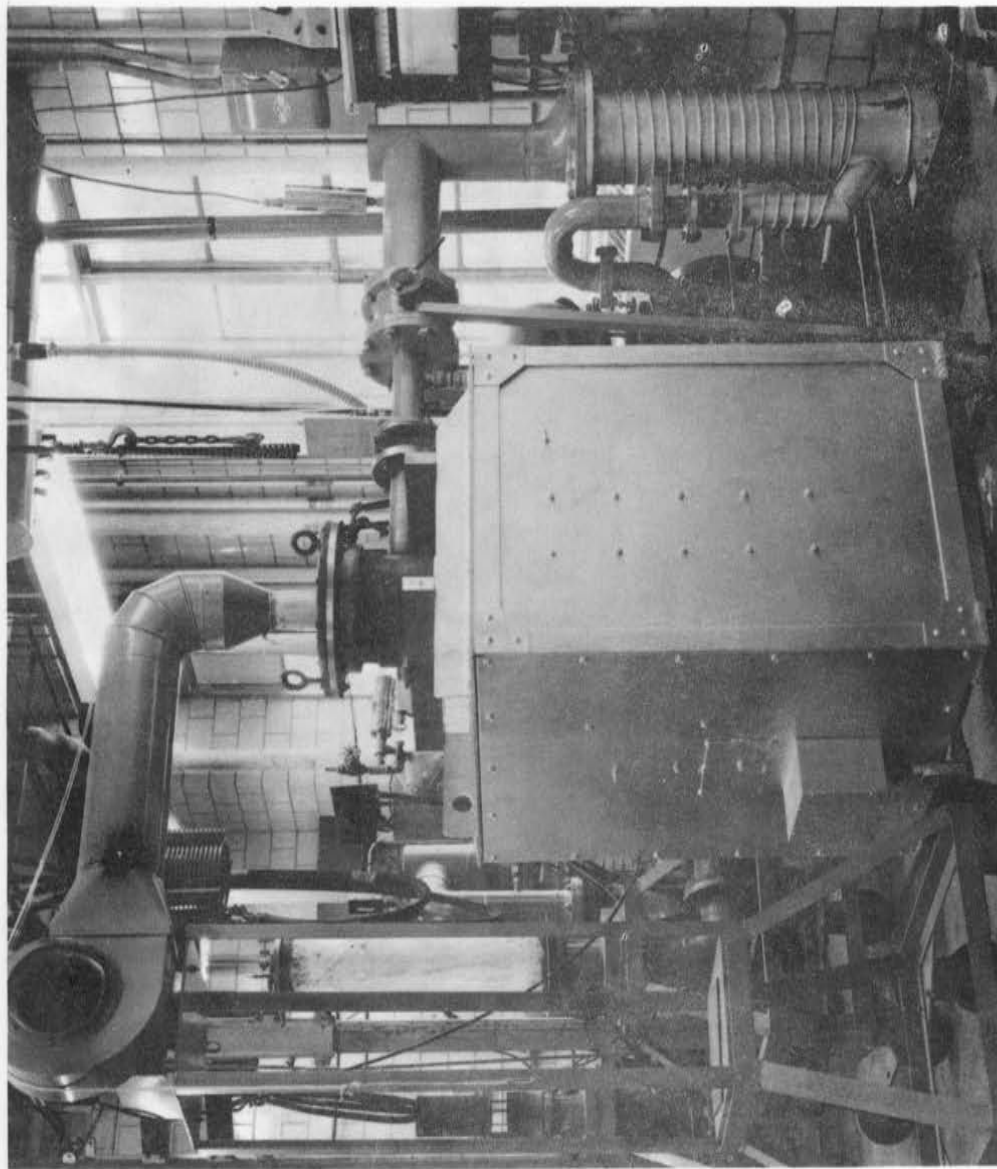


Fig. 53. Low Temperature Demagging Furnace and Retort.

thus providing a cold surface on which magnesium vapors are collected.

The vacuum system (lower right) consists of a National Research H-10-P diffusion pump backed by a Stokes 212 Microvac mechanical pump. The system was capable of maintaining a pressure of less than 0.03 microns on the retort at temperature. The demagging schedule consisted of heating at 900°C for a six-hour period followed by a 25-hour-hold at 950°C under a dynamic vacuum. Analysis of the sponge from four different large scale reductions showed that a uniform and reproducible product is obtained. A representative analysis in ppm is as follows: O₂, 350; Ca, 100; Mg, 100; F, 600; N₂, 75; C, 125 and Ti, 5000. It will be noted that as a result of the double heating and stirring operations the titanium pick-up is significantly higher than for the standard reduction. Should it be desirable to eliminate this crucible contamination, the use of a tantalum insert or liner has been successfully demonstrated by the small scale experiments.

The sponge was arc melted into ingots of various sizes for evaluation. The arc-melted ingots contained approximately 500 ppm oxygen. Since the magnesium, calcium and other volatile impurities are removed so completely by this demagging procedure, it was possible to vacuum arc melt the compacted sponge directly. This

gave an ingot with smooth sidewalls and very little evidence of the spattering encountered with the regular production grade sponge.

Evaluation of the fabricability of this high purity metal was done on several 5 lb arc-melted ingots. The ability of this material to be cold rolled was first tested. Specimens 1/4" thick cut from the ingots underwent 95% reduction in thickness, with edge cracking occurring after about 60% but showing no tendency of the cracks to propagate across the specimen. The cold rolling properties of a specimen containing 500 ppm O_2 were compared with those containing 2000 and 3000 ppm O_2 as is shown in Fig. 54. Figure 55 presents a comparison of the rolling properties, at 1000°F, of an ingot containing 500 ppm O_2 (C-332b) and one containing 1000 ppm O_2 (C-267b).

Two ingots were sent out for an evaluation of their extrusion properties. These were successfully extruded at 550°F (290°C) into complex shaped pieces having undergone an 8 to 1 reduction in one operation.

The hardness of this quality metal was measured in the arc-melted condition and after vacuum annealing at 900°C. The as-melted hardness was 50-55 BHN (500 Kg load) while that of the annealed specimen was 35-40 BHN.

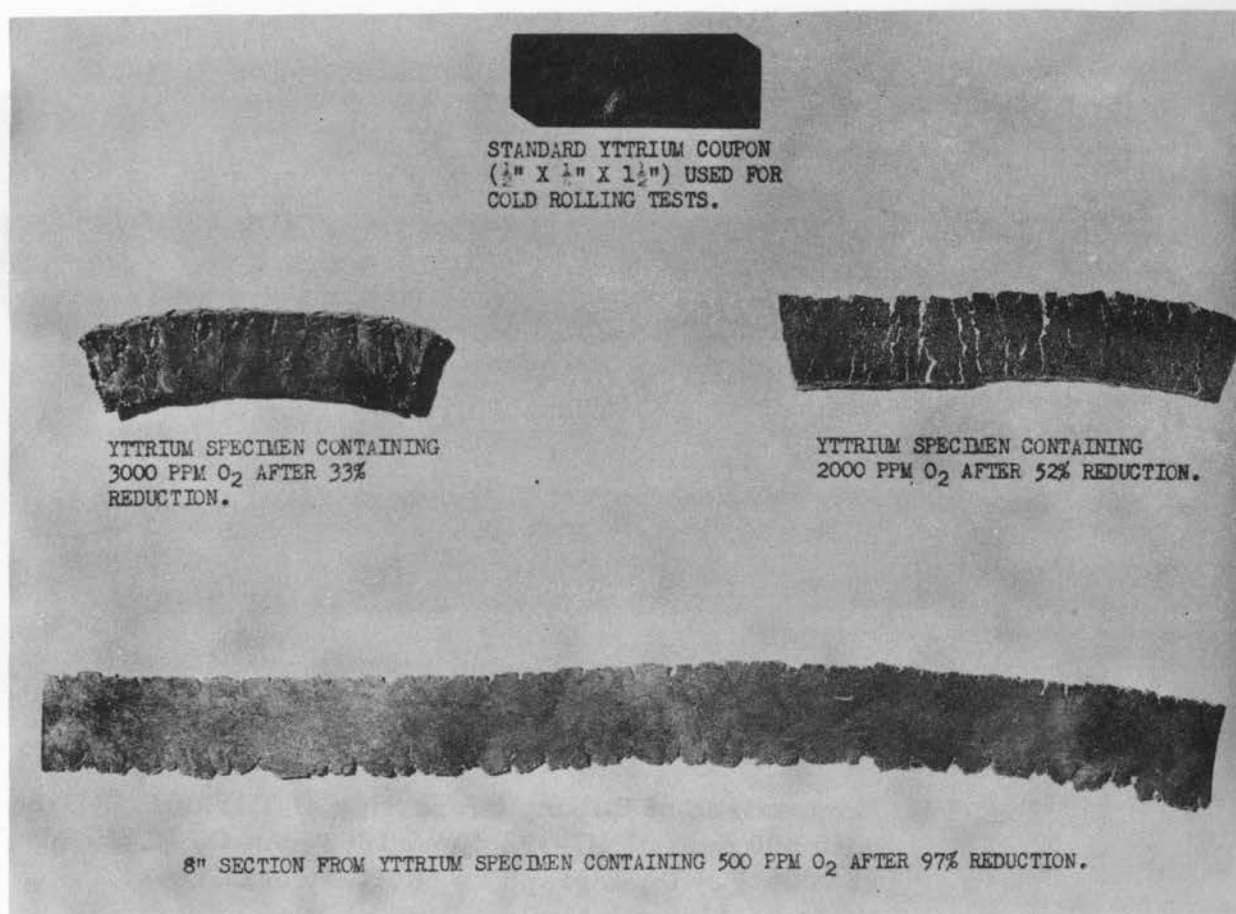


Fig. 54. Comparison of Cold Rolling Properties of Yttrium of Varying Oxygen Content.

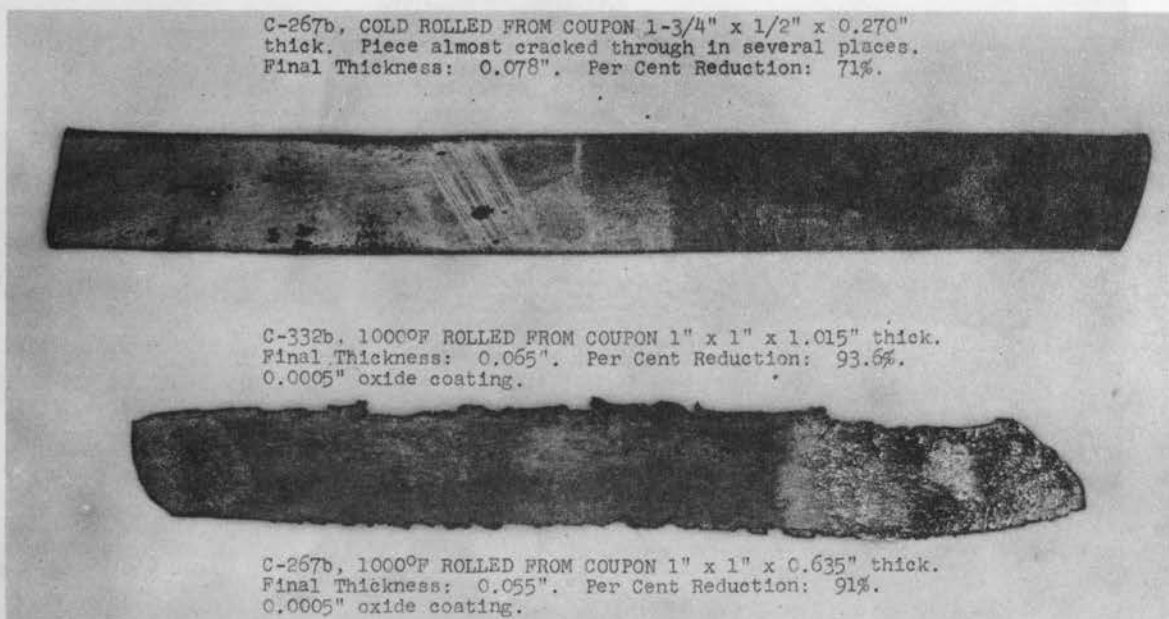


Fig. 55. Comparison of Rolling Properties of Yttrium with 500 ppm O₂ (C-332b) and 1000 ppm O₂ (C-267b) at 1000°F. Photograph by courtesy of General Electric Aircraft Nuclear Propulsions Laboratory.